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Thermal Analysis

When matter is heated, it undergoes certain physical and chemical changes. Physical changes include phase changes such as melting, vaporization, crystallization, transitions between crystal structures, changes in microstructure in metal alloys and polymers, volume changes (expansion and contraction), and changes in mechanical behavior. Chemical changes include reactions to form new products, oxidation, corrosion, decomposition, dehydration, chemisorption, and the like. These physical and chemical changes take place over a wide temperature range. The rates of chemical reactions vary with temperature and the properties of some materials, such as semicrystalline polymers and metal alloys, depend on the rate at which they are cooled. Materials are used over a wide range of temperatures, from Arctic cold to tropical heat, in corrosive environments, variable humidity, and under load (stress). It is necessary to characterize materials and their behavior over a range of temperatures to determine what materials are suitable for specific uses and to determine what temperature range materials or chemicals can withstand without changing. This sort of information is used to predict safe operating conditions for products, such as which type of tire material is best for vehicles in extremely cold or extremely hot climates, the average expected lifetime of materials such as paints and polymers exposed to temperature changes, processing conditions for materials, and the curing times and temperatures for dental filling material, among other uses.

The physical changes and chemical reactions a sample undergoes when heated are characteristic of the material being examined and the atmosphere in which the heating occurs. By measuring the temperature at which such reactions occur and the heat involved in the reaction, we can determine a great deal about the material. Composition of pure compounds and mixtures, including polymer blends, can be determined. The purity of pharmaceutical compounds can be determined. Rate of reaction, rate of crystallization, glass transition temperatures, decomposition temperatures, and catalysis can be studied. The effectiveness of additives and stabilizers in materials can be evaluated. Enthalpy changes (ΔH) of reactions can be measured. Percent crystallinity of polymers, which greatly affects the mechanical properties of polymers, can be determined. By heating materials under load (stress), mechanical properties such as modulus, ductility, yield point (the point at which nonpermanent elastic deformation changes to permanent plastic deformation), and volume change as a function of the load can be measured. These parameters are very important in engineering design to ensure safe and functional products.

The analytical techniques used to study changes in physical properties with temperature are called **thermal analysis** techniques. They include thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermometric titration (TT), and direct injection enthalpimetry, dynamic mechanical analysis (DMA), and thermomechanical analysis (TMA). Thermal analysis techniques are used in

the characterization of inorganic and organic compounds, polymers, cosmetics, pharmaceuticals, metals, alloys, geological samples, ceramics, glasses, and many manufactured products. Table 16.1 presents a brief overview of some applications for various thermal analysis methods. Table 16.2 lists some typical sample types and some of the properties that have been measured by thermal analysis methods.

16.1. THERMOGRAVIMETRY

Thermogravimetry or thermogravimetric analysis (TGA) measures the mass (weight) of a sample in a specified atmosphere as the temperature of the sample is programmed. The most common temperature program is a linear increase in temperature with time, although isothermal programs, stepped temperature programs, and so on can be used. In the most common TGA experiment, the sample temperature is increased linearly over a time period and the mass of the sample is constantly recorded. The output from a TGA experiment is a plot of mass (or mass%) vs. temperature. The TGA plot is called a **thermal curve**. An example of a TGA thermal curve for the decomposition of calcium carbonate is shown in Fig. 16.1. Weight or weight% is plotted along the y-axis and temperature (or time for a linear temperature ramp) along the x-axis. The change in weight of a sample as the temperature changes tells us several things. First, this determines the temperature at which the material loses (or gains) weight. Loss of weight indicates decomposition or evaporation of the sample. A gain in weight can indicate adsorption by the sample of a component in the atmosphere or a chemical reaction with the atmosphere. Second, the temperatures at which no weight change takes place are determined, which indicate the temperature stability of the material. These weight changes at certain temperatures are physical properties of chemical compounds under the conditions of the experiment (atmosphere, heating rate). This information can be used to determine if a sample is the same as a "standard" or "good" material in a production process, for example. Knowledge of the temperatures at which a sample is unstable and subject to decomposition or chemical change is important to the engineer because it reveals the temperature above which such materials as polymers, alloys, and building materials may not be used, as well as the temperatures at which they may be used safely.

Table 16.1 Some Applications of Thermal Analysis Methods

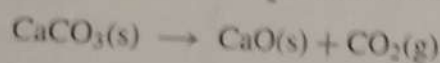
Applications	TGA	DSC, DTA	TMA	DMA
Compositional analysis	x	x		
Curing studies		x		x
Glass transition		x	x	x
Heat of reaction		x		
Oxidative stability	x	x		
Corrosion	x	x		
Creep			x	x
Stress relaxation			x	x
Thermal stability	x	x		
Viscoelastic properties			x	x
Protein denaturation		x		
Shrinkage			x	x

Table 16.2 Partial List of Sample Types and Properties Examined by Thermal Analysis

Properties	Samples						
	Chemicals	Elastomers	Explosives	Soils	Plastics	Textiles	Metals
Identification	x	x	x	x	x	x	x
Quantitative composition	x	x	x	x	x	x	
Phase diagram	x	x	x		x		x
Thermal stability	x	x	x		x	x	
Polymerization	x	x			x	x	
Catalytic activity	x						x
Reactivity	x	x			x	x	x
Thermochemical constants	x	x	x	x	x		x
Reaction kinetics	x	x	x		x	x	x

Note: x = Sample type that has been characterized for this property.

The weight lost by a sample heated to a given temperature helps the inorganic or analytical chemist to determine the composition of a compound and follow the reactions involved in its decomposition. It also enables the analytical chemist to identify crystals of unknown composition or determine the percentage of a given compound in a mixture of compounds. For example, if pure calcium carbonate (CaCO_3) is heated to 850°C , it loses 44% of its weight (Fig. 16.1). Also, the gas evolved can be collected and identified as CO_2 . This observation virtually confirms that the reaction



takes place at this temperature. How do we know this? If we know our sample was pure CaCO_3 and CO_2 is identified as a product of the reaction, the need for mass balance tells us

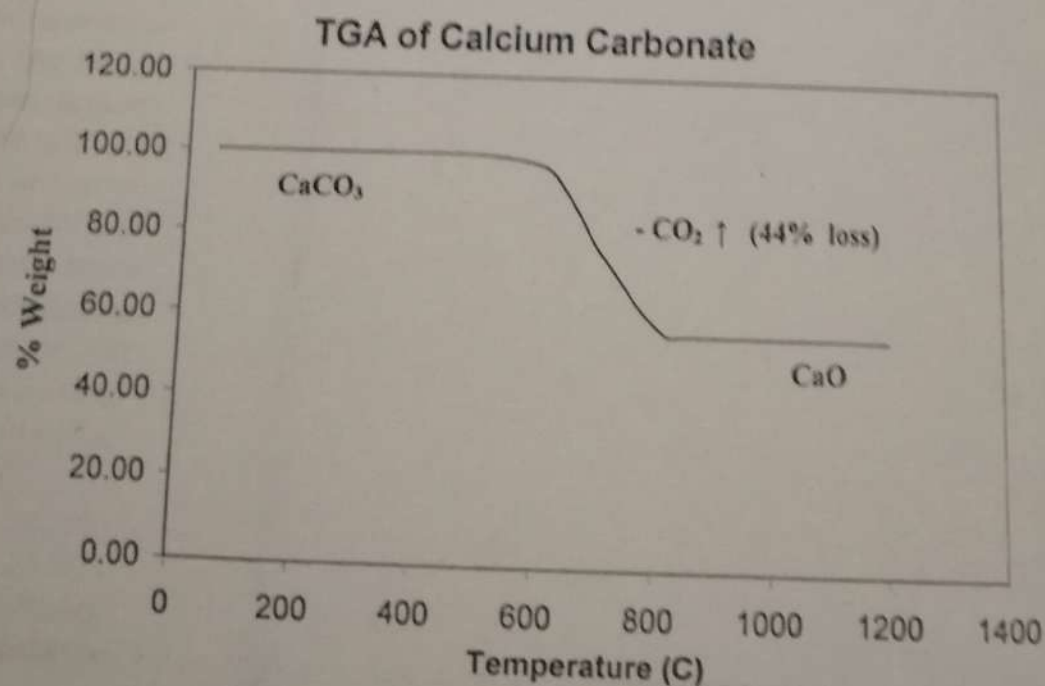


Figure 16.1 TGA thermal curve for pure anhydrous calcium carbonate, CaCO_3 . The loss in mass is due to the loss of CO_2 (g) and the compound remaining is CaO .

that CaO is a reasonable "other" product. If we had 50.0 mg of CaCO_3 to start with, the mass loss due to CO_2 can be calculated:

$$\text{mg CO}_2 = \frac{(50.0 \text{ mg CaCO}_3) \times (1 \text{ mmol CaCO}_3) \times (1 \text{ mmol CO}_2) \times (44.00 \text{ mg CO}_2)}{(100.09 \text{ mg}) (1 \text{ mmol CaCO}_3) (1 \text{ mmol CO}_2)}$$

$$\text{mg CO}_2 = 22.0 \text{ mg}$$

The loss of CO_2 equals a loss in weight of $(22.0 \text{ mg}/50.0 \text{ mg}) \times 100\% = 44\%$. From the stoichiometry, it is expected that 1 mole of CO_2 is lost for every mole of CaCO_3 present, which corresponds to a loss of 44% of the mass of 1 mole of CaCO_3 . The experimental mass loss supports the theoretical loss if the decomposition of CaCO_3 proceeds according to the reaction proposed. The formation of CO_2 can be verified by having the evolved gas analyzed by MS or by online IR spectroscopy. The CaO can be confirmed by analysis of the residue by XRD or other techniques.

The TGA technique was developed to solve problems encountered in gravimetric analysis. For example, a common precipitating and weighing form for the determination of calcium was calcium oxalate. In practice, the calcium oxalate was precipitated, filtered, and the filtrate dried and weighed. The drying step was difficult to reproduce. A particular procedure might recommend drying at 110°C for 20 min and cooling prior to weighing. The analyst would then obtain very reproducible results derived from his or her own work. A second procedure might recommend drying at 125°C for 10 min, cooling, and weighing. As before, the analyst using this method would obtain very reproducible results, but these results might not agree with those of the first research worker. The thermal curve of hydrated calcium oxalate is shown in Fig. 16.2. When we examine the

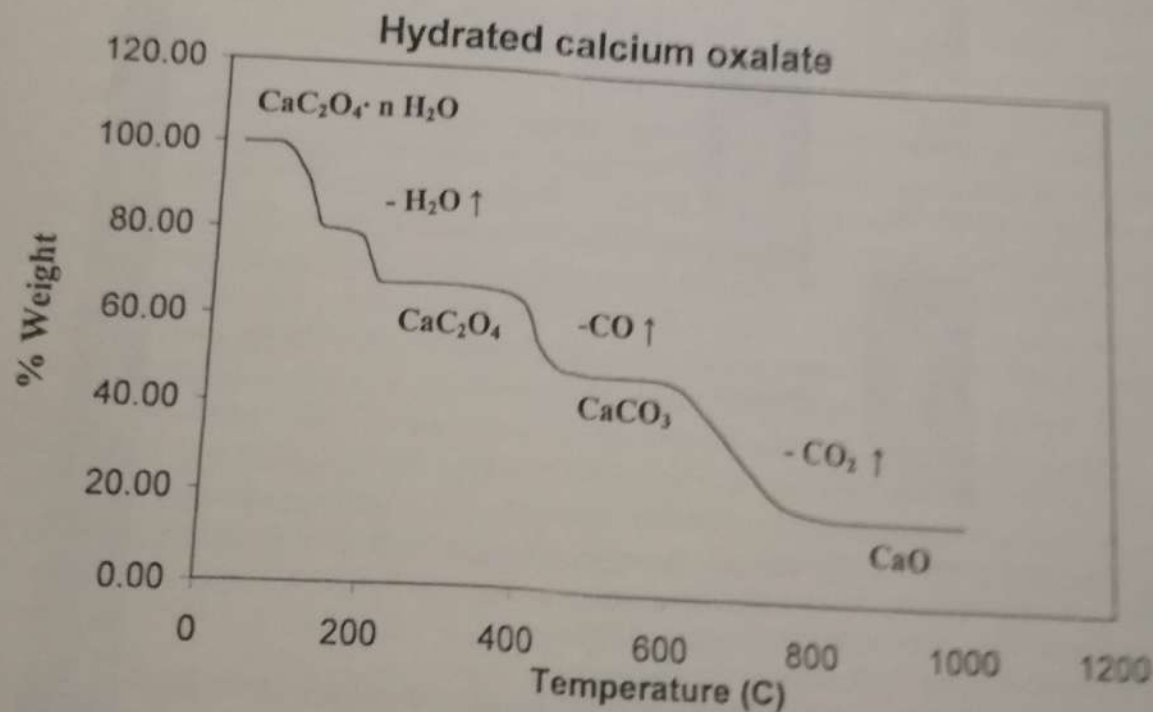


Figure 16.2 TGA thermal curve of hydrated calcium oxalate, $\text{Ca}(\text{COO})_2 \cdot x\text{H}_2\text{O}$, with both adsorbed water from the precipitation process and water of crystallization. There is a loss of adsorbed water starting at about 90°C , and loss of bound water at about 150°C . The stable compound above 225°C is anhydrous calcium oxalate, $\text{Ca}(\text{COO})_2$. This loses CO at about 450°C to form CaCO_3 . The calcium carbonate is stable until approximately 600°C , when it loses CO_2 to form CaO. (Compute this step with Fig. 16.1.)

thermal curve, we find that calcium oxalate loses weight over a range of temperatures from 100°C up to 225°C. The most logical explanation for this weight loss is that water is evaporating from the sample. The water that is driven off includes not only absorbed or adsorbed water from the precipitating solution, but also water of crystallization (also called water of hydration) that is bound to the calcium oxalate as $\text{CaC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$. It is only when both types of water are driven off that reproducible results are achievable. If the sample were heated to 110°C, the absorbed water would be driven off, but a small amount of bound water (i.e., water of crystallization) would also be lost. Similarly, if the drying temperature were 125°C, the absorbed water would be driven off and a different small amount of bound water would be lost. As long as a drying temperature was rigidly adhered to, the results would be reproducible, but results using different drying temperatures would show differences because the amount of bound water lost would vary. The TGA experiment shows that drying to a temperature above 225°C but below 400°C will result in a stable form suitable for gravimetric analysis.

16.1.1. TGA Instrumentation

Modern TGA equipment has a sensitive balance, usually a microbalance, for continuously measuring sample weight, a furnace surrounding a sample holder, and a purge gas system for providing inert or reactive atmospheres. A computer generally controls the furnace and the data (weight vs. sample temperature) is collected and processed by computer. Intelligent autosamplers are available for most instruments that permit the unattended analysis of samples.

Modern analytical microbalances of several different designs are commercially available—torsion balances, spring balances, and electrobalances have been used in TGA instruments. In general, the balance is designed so that a change in sample weight generates an electrical signal proportional to the weight change. The electrical signal is transformed into weight or weight loss by the data processing system and plotted on the y-axis of the thermal curve. TGA balances are available for sample masses from 1 to 1000 mg, with the usual sample weighing between 5 and 20 mg. There are specialized high-capacity TGA systems available that can accommodate samples of up to 100 g and systems that can handle microgram quantities of sample. Figures 16.3 and 16.4 show the schematic of a TGA electrobalance and a cutaway of a commercial high-capacity TGA based on the electrobalance. The usual sample size for TGA is very small, so care must be taken to obtain a homogeneous or representative sample. The balance itself must be thermally isolated from the furnace, although the sample holder and sample must be in the furnace. There are two possible configurations of the balance and furnace, a horizontal furnace or a vertical furnace. Both types of configuration suffer from drift as the temperature increases. Vertical configurations suffer from buoyancy effects due to the change in gas density with temperature. The horizontal configuration was designed to minimize buoyancy effects, but horizontal configurations experience changes in the length of the quartz rod connecting the sample to the balance as the temperature changes. Buoyancy effects and changes in the quartz rod result in error in determining the mass of the sample.

The furnace surrounds the sample and sample holder. It must be capable of being programmed for a linear heating rate. Modern instruments can be heated and cooled rapidly, which increases sample throughput. Instruments that heat at rates of up to 1000°C/min are available. One commercial instrument can heat at rates up to 200°C/min from room temperature to about 1200°C; cooling by forced air can be done at ~50°C/min. There are furnaces available with upper temperatures of 1500°C,

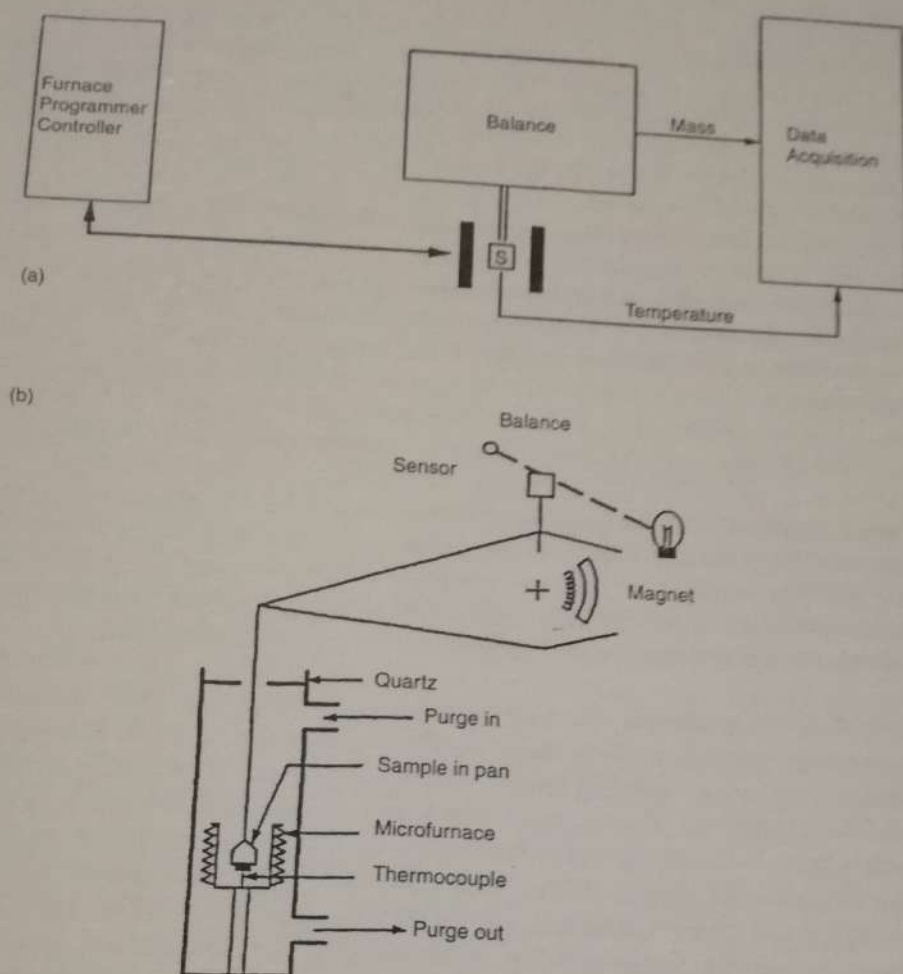


Figure 16.3 (a) Block diagram of a TGA system. S represents the sample pan hanging from the balance arm in position in the furnace (represented by the solid bars on each side). (b) Schematic of a commercial TGA, showing the purge gas inlet and outlet and the thermocouple position beneath the sample pan. [Figure 16.3(b) courtesy of PerkinElmer, Inc. Shelton, CT. www.perkinelmer.com.]

1700°C, or 2400°C; these higher temperature instruments are useful for studying refractory materials and engineering materials. The furnace must be able to be purged with a desired gas, to provide the correct atmosphere for the experiment and to remove gaseous products from the sample compartment. Argon or nitrogen is used when an inert atmosphere is desired. Reactive gas atmospheres can be used for certain studies. Air is often used for oxidation and combustion studies. Hydrogen gas may be used to provide a reducing atmosphere, with the appropriate precautions to prevent explosions. Modern instruments permit the purge gas to be switched automatically, so that the sample can start heating in an inert atmosphere and be switched to air or other reactive gas at high temperatures, for example.

The sample holder and any instrument parts inside the furnace, such as the thermocouple for measuring the temperature, must be able to withstand high temperature and be

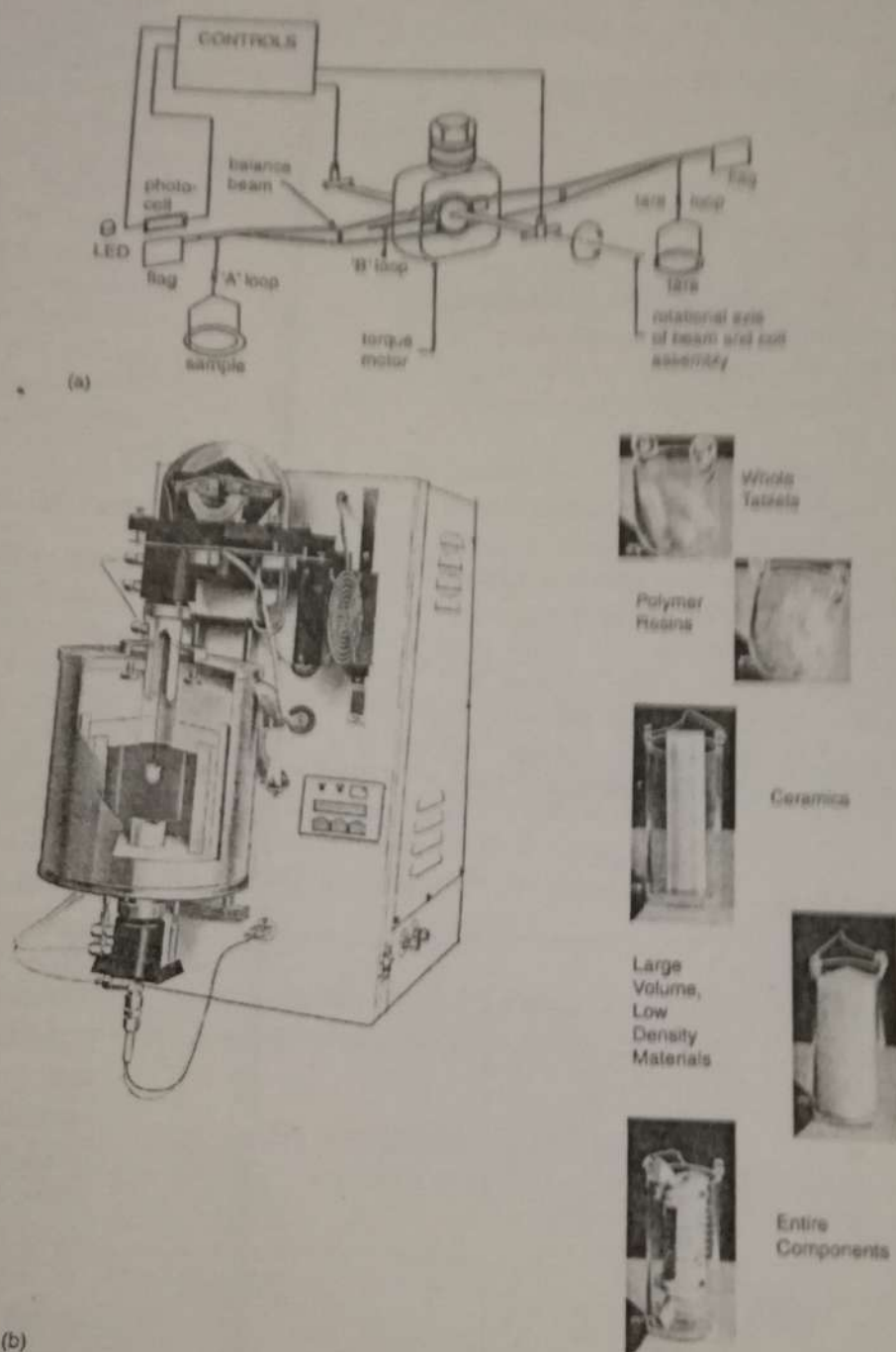


Figure 16.4 (a) Electrobalance for a TGA. As the sample weight changes, the balance arm tips, resulting in a change in the amount of light reaching the photocell. This generates a current to restore the arm position; the current is proportional to the change in weight of the sample. (b) Cutaway view of a high-capacity TGA capable of holding 100 g samples. Typical types of large samples in quartz sample holders are shown in the photographs on the right. (Courtesy of ThermoCahn, Madison, WI, www.thermo.com.)

inert at these high temperatures. Quartz, platinum, and various ceramics are used for the sample holder and other parts. The sample is placed in a small pan or crucible made of Pt, quartz, or ceramic.

Ideally, the temperature recorded is the exact temperature of the sample. This entails measuring the temperature of the sample while the analysis is carried out. It is particularly

important to measure the temperature of the sample rather than that of the furnace. This is difficult because the temperature is measured with a thermocouple that is near but not in the sample. The temperature of the sample inside the furnace is measured with a thermocouple, either a chromel/alumel thermocouple or one made of Pt alloy. The thermocouple is never inserted directly into the sample because of possible sample contamination (or contamination of the thermocouple resulting in errors in temperature), inadvertent initiation of a catalytic reaction, particle size effects, sample packing effects, and possible weighing errors. The thermocouple is made as small as possible and placed close to the sample holder, sometimes in contact with the bottom of the sample pan. The temperature actually recorded may be slightly different from the sample temperature; the sample temperature generally is lower than the temperature recorded by the thermocouple. This is due to factors such as rate of heating, gas flow, thermal conductivity of the sample, and the sample holder. Modern instruments have a temperature-voltage control program in the computer software that permits reproducible heating of the furnace. With precise, reproducible heating, the thermocouple can be calibrated to provide accurate furnace temperatures, but the relationship between actual sample temperature and recorded temperature is complex. The problem is compounded by the fact that at temperatures below 500°C, most of the heat transferred from the furnace to the sample takes place by convection and conduction, but at temperatures above 500°C, where the furnace is red-hot, most of the energy is transferred by radiation. The switch from conduction-convection to radiative energy transfer makes choosing the position of the thermocouple to obtain accurate temperature measurements of the sample quite a complicated problem.

Temperature calibration of TGA instruments with samples of pure materials with well-characterized weight losses can be done, but often is not satisfactory. For example, one problem with this approach is that black samples such as coal behave differently from white samples such as calcium phosphate under the influence of radiant energy, and the sample temperatures will therefore be different under the same furnace conditions. A more accurate calibration method uses the Curie temperature of various ferromagnetic standard materials. The materials undergo specific and reversible changes in magnetic behavior at their Curie temperature. Standards are available covering the temperature range of 242–771°C. A **ferromagnetic material** is magnetic under normal conditions, but at a characteristic temperature (**the Curie temperature**) its atoms become disoriented and paramagnetic and the material loses its magnetism. To take advantage of this phenomenon, we weigh the ferromagnetic material continuously, with a small magnet placed above the balance pan. The standard's apparent weight is then its gravitational weight minus the magnetic force it experiences due to the magnet immediately above. At the Curie temperature, the standard loses its magnetism and the effect of the magnet is lost. There is a change in the apparent weight of the standard, and this can be recorded. The temperatures of the Curie transitions of ferromagnetic materials are well known and therefore can be used for calibration purposes. An example of calibration using the Curie temperatures of alumel and nickel is shown in Fig. 16.5.

16.1.2. Analytical Applications of Thermogravimetry

One of the first important applications of thermogravimetry was the determination of correct drying temperatures for precipitates used in gravimetric analysis. This knowledge was of vital importance if accurate and reproducible results were to be obtained from gravimetric analysis. A second important application was the identification of the gases given off while a sample's temperature is increased. In addition, the composition of the residue can be determined using techniques such as XRD, XRF, and other techniques.

Thermal Analysis

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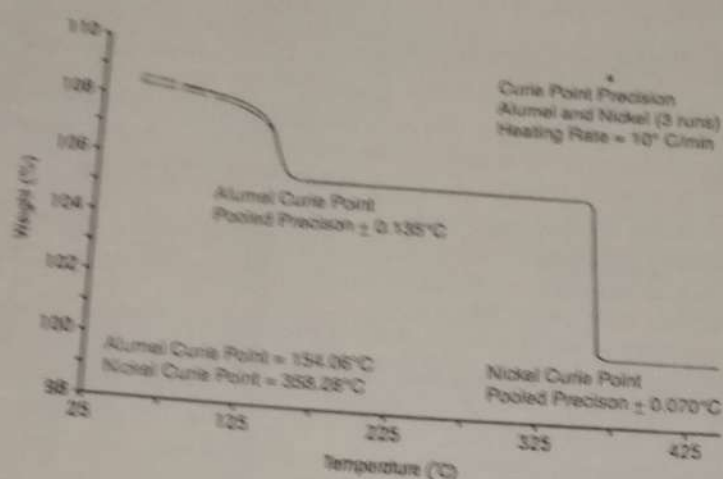


Figure 16.5 The TGA Curie point method records for each standard an apparent sharp weight change at a well-defined temperature, which corresponds to a known transformation in the standard's ferromagnetic properties at that temperature. The figure shows the relative temperature precision from three replicate calibration runs using alumel and nickel Curie point standards. (Courtesy of TA Instruments, New Castle, DE, www.tainst.com.)

This information reveals the chemical decomposition process occurring when materials are heated and permits identification of the formulas of the starting materials. TGA is very important in determining the upper use temperatures of materials such as polymers by identifying the temperature at which oxidative degradation occurs on heating in air.

From Fig. 16.6 it can be determined that when pure calcium oxalate monohydrate, $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}(\text{s})$, is heated, it first loses water of crystallization and forms $\text{Ca}(\text{COO})_2(\text{s})$.

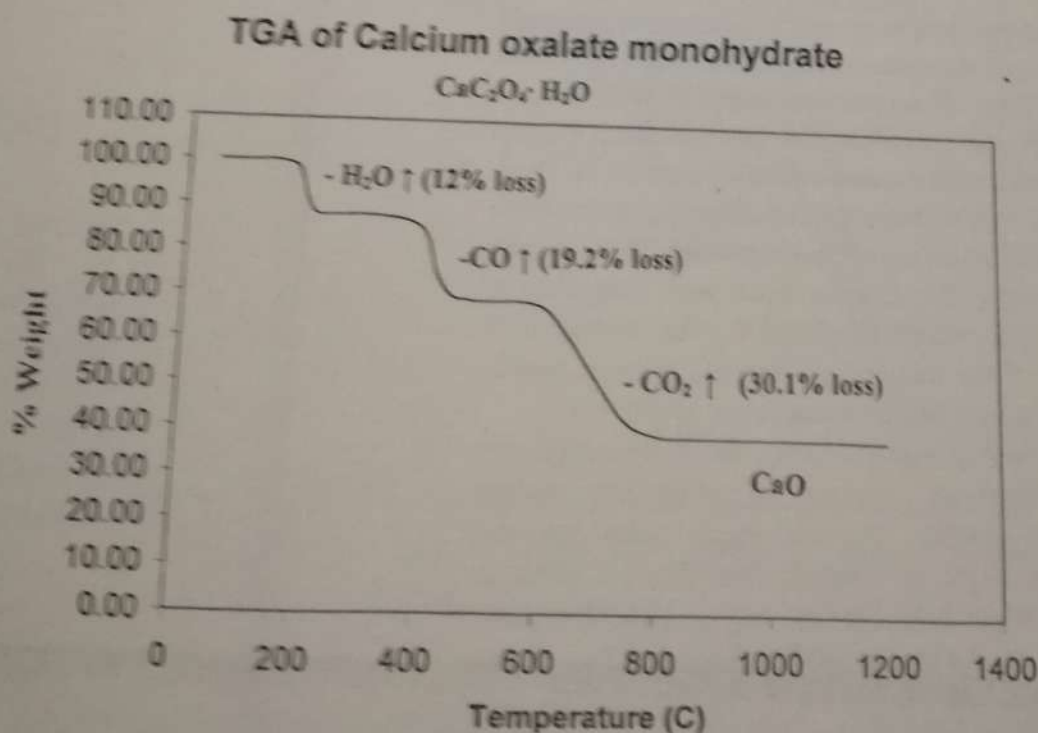
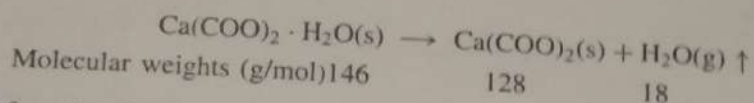


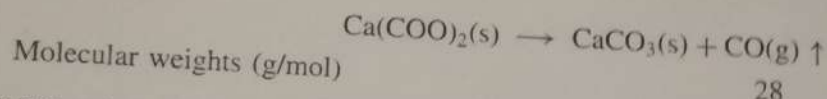
Figure 16.6 TGA thermal curve of calcium oxalate monohydrate, $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$.

The fact that the compound contains only 1 mole of water of hydration can be determined from the mass loss. The reaction is:



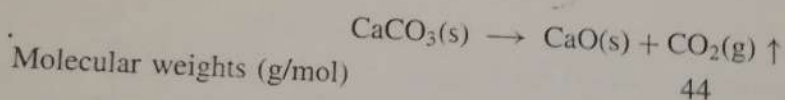
Therefore the %W lost = $(18/146) \times 100 = 12.3\%$. If our initial sample mass was 20.00 mg, the mass loss at the first step would be 2.46 mg if there is 1 mole of water of crystallization. If the mass loss actually measured was 4.92 mg, that would mean there were 2 moles of water of crystallization and the formula would be $\text{Ca(COO)}_2 \cdot 2\text{H}_2\text{O(s)}$, a dihydrate.

Upon further heating up to about 400°C , CO(g) is given off and the reaction that occurs is:



The %W lost from the initial compound = $(28/146) \times 100 = 19.2\%$. The total %W lost at this point is the sum of the two steps, $12.3 + 19.2 = 31.5\%$.

Finally, at even higher temperatures (about 800°C), the CaCO_3 formed at 400°C decomposes:



The %W lost from the original compound = $(44/146) \times 100 = 30.1\%$. The total mass loss is the sum of all three steps: $12.3 + 19.2 + 30.1 = 61.6\%$. The losses correspond to what is seen in the decomposition of calcium oxalate monohydrate in Fig. 16.6. The \uparrow symbol indicates gas evolved from the sample and swept out of the TGA system. The gases may be identified if the TGA analyzer is connected to an IR spectrometer or a mass spectrometer.

TGA can be used for the identification of compounds present in mixtures of materials. When such mixtures are heated using a thermogravimetric analyzer, the thermal curve produced consists of all possible weight losses from all components superimposed on each other. Interpretation of the complete thermal curve requires that the individual thermal events be separated and identified. In many cases, the components of the mixture can be identified and a quantitative determination of each is possible from the thermal curve. An example of how this can be done is shown in Fig. 16.7. The uppermost curve is the weight loss curve for pure compound A. The next lower curve is the weight loss curve for pure compound B. The bottom curve is the weight loss curve for a mixture of A and B. The amount of A present in the mixture can be determined from the weight loss between points δ and ϵ , while the amount of B is determined from the weight loss between points β and γ .

An illustration of the application of TGA to quantitative analysis of mixtures is the determination of the magnesium oxalate content of a mixture of magnesium oxalate and magnesium oxide, MgO . Magnesium oxalate is less stable than calcium carbonate; it decomposes to magnesium oxide, MgO , at $\sim 500^\circ\text{C}$. Pure MgO is stable at room temperature and to well above 500°C ; MgO does not lose any weight. The TGA curve for this mixture shows two mass losses, one at about 200°C . The second mass loss occurs in the $397\text{--}478^\circ\text{C}$ range. Thinking about what happened to calcium oxalate, it is reasonable to suppose that the first mass loss is due to loss of water, both adsorbed and water of crystallization. From the formula for $\text{Mg(COO)}_2 \cdot 2\text{H}_2\text{O}$, we see that there

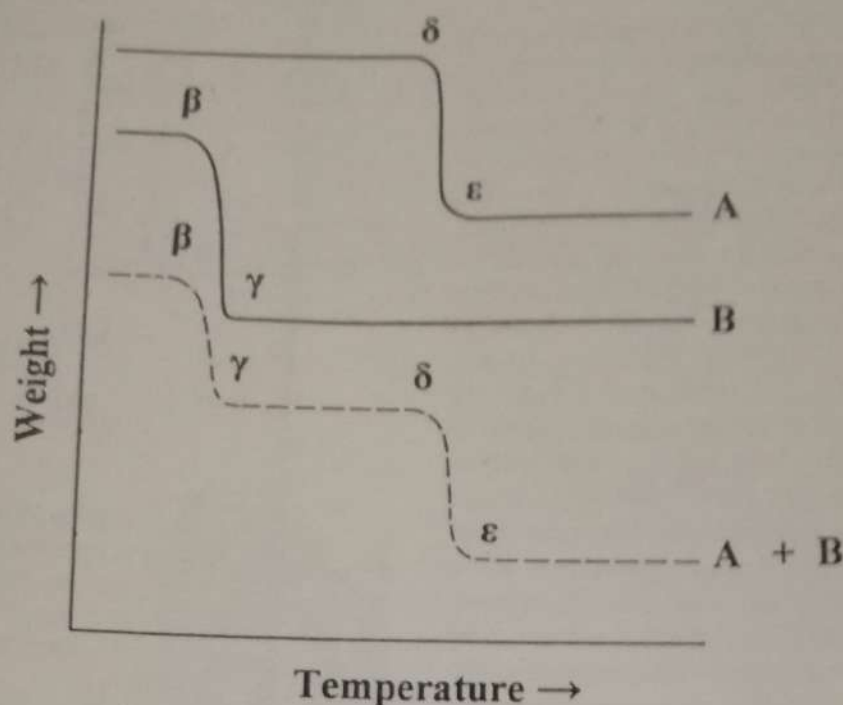
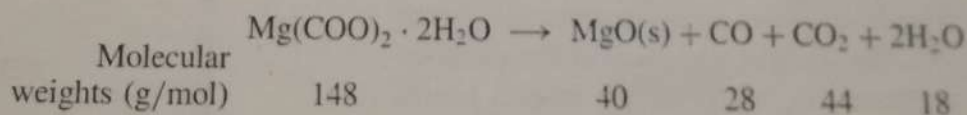


Figure 16.7 TGA thermal curves for (top) pure A, (middle) pure B, and (bottom dotted line) a mixture of A and B. Because A and B have unique temperatures at which mass is lost, the composition of the mixture may be determined.

are 2 moles of water of crystallization for every mole of magnesium oxalate. Only one other mass loss is seen, and we know MgO is stable at these temperatures. We can assume that when $\text{Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$ is heated to a temperature above 500°C , it forms MgO according to the reaction:



The final weight loss is therefore: $\%W = [(28 + 44 + 2(18))/148] \times 100 = 73\%$

We would lose 73 mg for every 100 mg of pure magnesium oxalate dihydrate we had in the mixture on heating the mixture to 500°C . Note that the decomposition of magnesium oxalate does not follow the same process as the decomposition of calcium oxalate. Calcium oxalate first forms calcium carbonate, which only loses carbon dioxide to form CaO at temperatures above 600°C . Magnesium oxalate appears to decompose directly to MgO in one step at about 500°C . The weight remaining from the magnesium oxalate is equal to:

$$\begin{aligned} & \frac{\text{mol wt MgO}}{\text{mol wt Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O}} \text{ per gram of Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O} \\ &= \left(\frac{40}{148} \right) = 0.27 \text{ g MgO/g Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O} \end{aligned}$$

The following data were obtained from our TGA curve:

Original weight of sample	25.00 mg
Weight of sample after heating to 500°C	10.40 mg
Loss in weight	14.60 mg

But we have already calculated that $\text{Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$ loses 73% of its mass upon heating to 500°C; therefore the weight of $\text{Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in the original sample was:

$$\text{mg } \text{Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O} = (14.60 \text{ mg lost}) \frac{100 \text{ mg } \text{Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O}}{73 \text{ mg lost}} = 20 \text{ mg}$$

Then the concentration of $\text{Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in the original sample was:

$$\% \text{Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O} = \frac{\text{mg } \text{Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O}}{\text{total sample weight in mg}} \times 100$$

$$\% \text{Mg}(\text{COO})_2 \cdot 2\text{H}_2\text{O} = \frac{20 \text{ mg}}{25.00 \text{ mg}} \times 100 = 80\%$$

Thus the other 20% of the starting mixture is MgO .

Similarly, we can determine the magnesium oxalate content and the calcium oxalate content in a mixture of the two compounds. The TGA curve of the mixture is shown in Fig. 16.8. We have already seen in Fig. 16.6 that calcium carbonate decomposes to calcium oxide above 600°C. We can deduce from the thermal curve for magnesium oxalate that magnesium carbonate is not stable because the oxalate decomposes directly to MgO . So at temperatures above 500°C, but below 600°C we should have a mixture of MgO and CaCO_3 . Above 850°C the CaCO_3 will have decomposed to CaO , so the

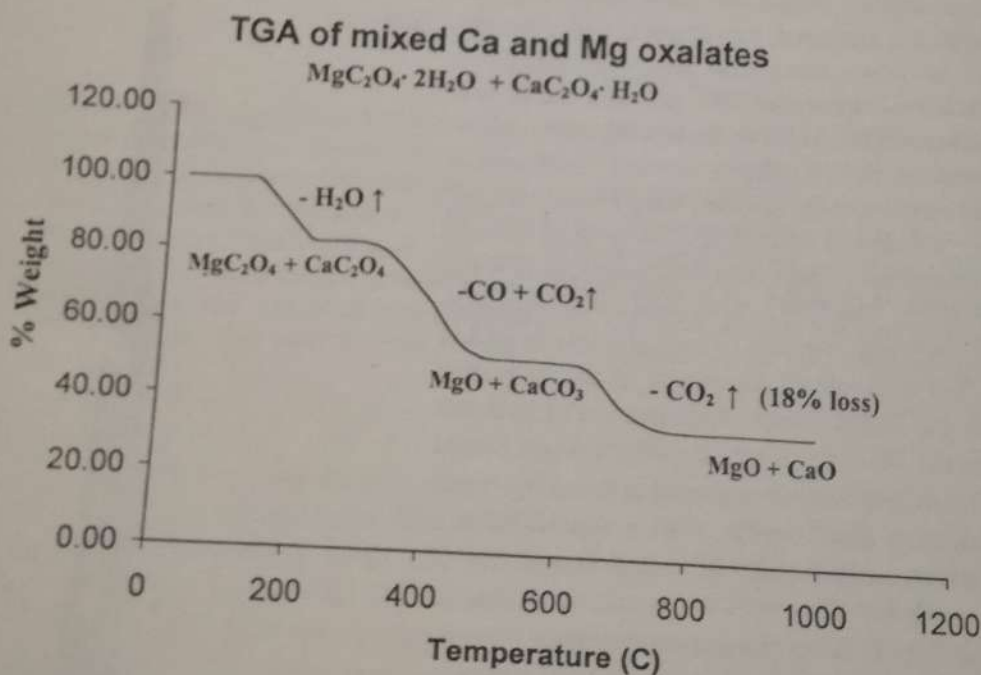


Figure 16.8 TGA thermal curve of a mixture of calcium oxalate monohydrate and magnesium oxalate dihydrate. The last weight loss is due to the loss of CO_2 only from calcium oxalate monohydrate. Therefore, the composition of the mixture can be determined, even though the other steps have combined mass losses from both compounds.

residue is a mixture of CaO and MgO. By examining Fig. 16.6 and the information we have above on the magnesium salt, it is evident that the weight loss in Fig. 16.8 above 600°C is due to the evolution of CO₂ from the CaCO₃ that came from the Ca(COO)₂·H₂O. We know one molecule of Ca(COO)₂·H₂O generates one molecule of CO₂. If the weight loss above 600°C (due to CO₂ loss) was 18%, then the weight% of Ca(COO)₂·H₂O in the mixture is

$$\frac{\text{mol wt Ca(COO)}_2 \cdot \text{H}_2\text{O}}{\text{mol wt CO}_2} \times 18\% = \frac{146}{44} \times 18\% = 60\%$$

Assuming that the weights of calcium oxalate and magnesium oxalate total 100%, then it follows that the percentage of Mg(COO)₂·2H₂O = 100 - 60 = 40%. As you can see from the examples given, TGA can be used for quantitative analysis, but not without some knowledge of the sample. If there were other components in our mixture of oxalates that we did not know about, our assumption that the two oxalates composed 100% of the sample would be wrong. If there is another component that loses weight above 600°C we have another error. Without some knowledge of the sample, our calculated value for one (or both) of the components could be wrong.

TGA also provides quantitative information on organic compound decompositions, and is particularly useful for studying polymers. An example is the use of TGA to determine the amount of vinyl acetate in copolymers of vinyl acetate and polyethylene. On heating, each mole of vinyl acetate present loses 1 mole of acetic acid. A TGA study of several vinyl acetate-polyethylene copolymers is presented in Fig. 16.9.

TGA is very useful for providing qualitative information about samples of many types. TGA can provide qualitative information on the stability of polymers when they are heated in air or under inert atmospheres. From the decomposition temperatures of various polymers heated in a TGA in an air atmosphere, the upper use temperatures of

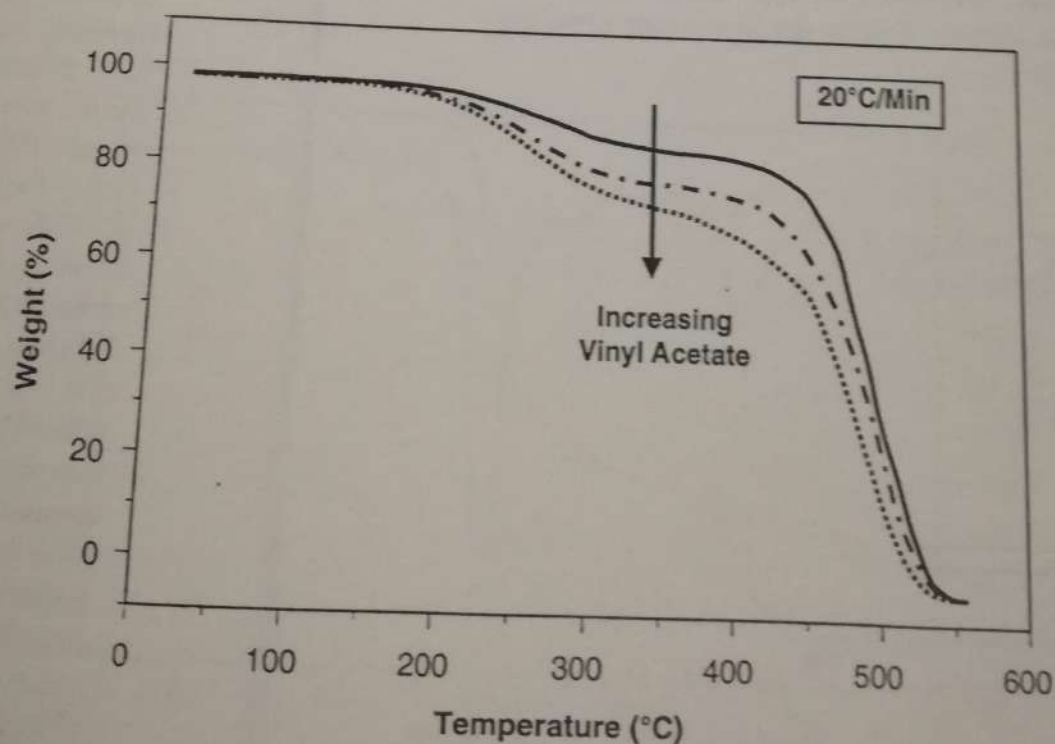


Figure 16.9 TGA thermal curves of vinyl acetate copolymers. The weight loss at 340°C is due to loss of acetic acid and gives a quantitative measure of the amount of vinyl acetate in the polymer. (Courtesy of TA Instruments, New Castle, DE, www.tainst.com.)

polymer materials can be determined. Figure 16.10 presents the decomposition temperatures for a variety of common polymeric materials; such a TGA comparison can be used to choose a polymer that will be stable below a certain temperature for a given application.

Another example of the application of thermogravimetry is in the characterization of coal. A TGA thermal curve for a coal sample heated in nitrogen or some other inert atmosphere indicates, in a single analysis, the percentage of volatiles present and the "fixed carbon"; if the atmosphere in the TGA is then automatically switched to air, the fixed carbon will burn and the amount of ash in the coal is determined as the residue left. This is very valuable information in the characterization of the quality of the coal and for its handling and subsequent use. Coals vary in their volatiles content and in their carbon content. Coals often contain a considerable amount of volatile material. The composition of this volatile material is variable and may contain valuable chemicals that can be used in the pharmaceutical industry, the dyestuff industry, and the chemical industry. Of course it can be used as a fuel, "coal gas". The newest form of carbon to be discovered, C_{60} , called buckminsterfullerene, and related fullerene compounds are found in soot. TGA can be used to characterize soot for its fullerene content, as the fullerenes are more volatile than graphite. Similarly, nonvolatile additives in polymers can be measured quantitatively by TGA. The pigment additive "carbon black", which is not volatile, is measured in a sample of nylon polymer, shown in Fig. 16.11. The polymer is burned off and the nonvolatile pigment determined by the mass remaining. Other polymer additives such as silica, titanium dioxide, and inorganic pigments such as cadmium red, and nonvolatile flame-retardants can be measured in a similar manner.

A high-precision TGA may be used under isothermal or nonisothermal conditions as a mass detector to study kinetics. Such an approach has been used to study oxidation of metals, corrosion, rates of reaction involving mass changes, and phase changes involving small changes in oxygen content for materials like high-temperature superconductors. Many applications of TGA can be found in the scientific literature and on the websites of thermal analysis instrument manufacturers. Websites with applications include the TA Instruments site at www.tainst.com, the Mettler-Toledo site at www.mt.com, and the PerkinElmer site at www.perkinelmer.com.

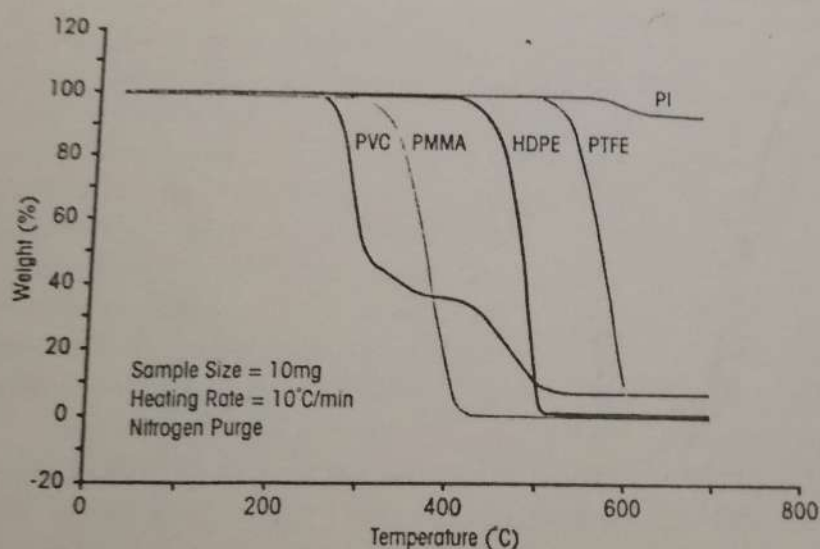


Figure 16.10 TGA thermal curves showing the decomposition temperatures of some common polymers: PVC, polyvinylchloride; PMMA, polymethylmethacrylate; HDPE, high-density polyethylene; PTFE, polytetrafluoroethylene; PI, polyimide. (Courtesy of TA Instruments, New Castle, DE, www.tainst.com.)

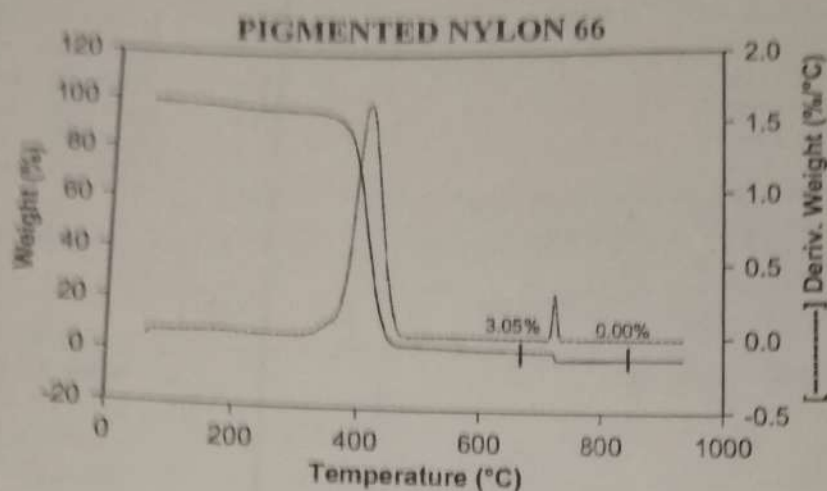
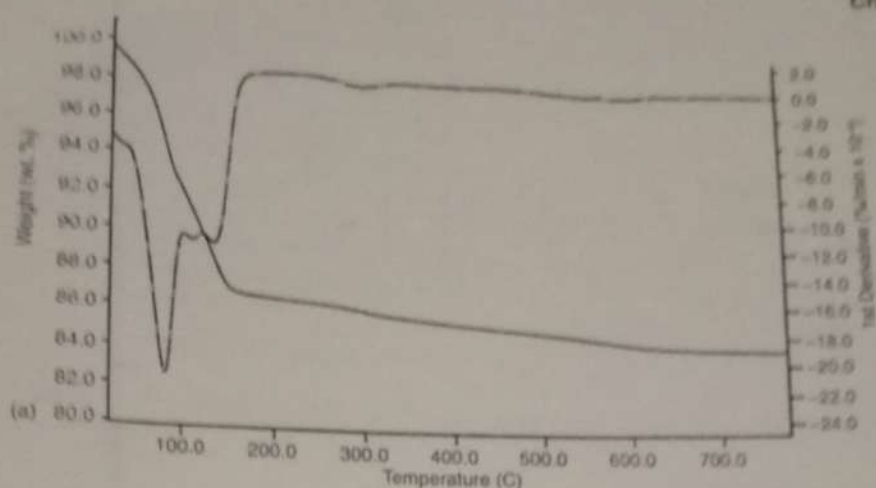


Figure 16.11 TGA determination of carbon black pigment in nylon. The sample was heated under nitrogen up to 650 °C, and then the purge gas was automatically switched to air. The polymer decomposes between 350 °C and 450 °C, leaving the carbon black pigment, which will not decompose in nitrogen, as the 3.05% by weight residue. On switching to air, the entire residue decomposes (final mass of 0.00%). This shows that the entire sample including the pigment was organic in nature. The solid line is the thermal curve, while the dotted line is the first derivative (DTG) plot. (Courtesy of TA Instruments, New Castle, DE, from Thermal Analysis Applications Brief TA-122.)

16.1.3. Derivative Thermogravimetry

Examination of a TGA curve will show that a sample's weight loss associated with a particular decomposition occurs over a considerable temperature range, not at a single temperature. When TGA is used to identify an unknown compound, this wide range is a handicap because the uncertainty of identification is increased. This problem can be partially overcome by derivative thermogravimetry (DTG). In DTG, the first derivative of the TGA curve is plotted with respect to temperature. The plot that results has the change in weight with time, $d(w)/dt$, which is the rate of weight change, on the y-axis. Figure 16.12(a) shows the TGA curve and its DTG curve for a hydrated sodium silicate, general formula $\text{Na}_x\text{Si}_y\text{O}_z \cdot n\text{H}_2\text{O}$. From the TGA curve, the temperature range over which the loss of water occurs is broad and does not have a smooth slope. The DTG curve shows that three separate steps occur in the range of 50–200 °C, all probably due to loss of water bound in different ways to the sodium silicate. Another example of the power of the derivative plot is shown in Fig. 16.12(b). This is a TGA and its DTG curve for a mixture of hydrated salts of barium, strontium, and calcium. From the TGA, there appears to be a single weight loss occurring between 130 °C and 210 °C. This might be misinterpreted to be a single pure compound if all we had was the TGA thermal curve. But from the very sensitive DTG, it is clear that there are three different losses of water, occurring at 140 °C, 180 °C, and 205 °C, respectively. These peaks are in fact loss of water first from the barium salt, then from the strontium salt and finally from the calcium salt. The DTG gave us a clue that more than one event was taking place, a clue that the TGA did not provide. Consequently, DTG is a valuable method of data presentation for thermal analysis. A similar example of the power of the DTG plot is shown in Fig. 16.13, which shows desorption of chemisorbed basic compounds from the acidic sites of a zeolite catalyst. **Zeolites**, an important class of catalysts, are porous crystalline aluminosilicates with acidic sites. The number and relative strength



(b)

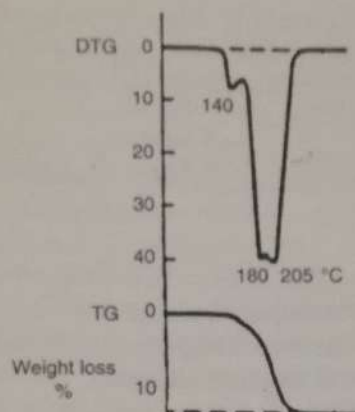


Figure 16.12 (a) TGA (solid line) and DTG (dotted line) thermal curves of a pure hydrated sodium silicate. The TGA mass loss from 50–150°C suggests loss of water in more than one form because of the change in slope seen during the step. The first derivative DTG plot clearly shows three separate mass losses due to water bound in different forms. (Courtesy of PerkinElmer, Inc. Shelton, CT, www.perkinelmer.com.) (b) Partial TGA (bottom curve) and DTG (top curve) thermal curves for a mixture of hydrated barium, strontium, and calcium oxalates. L. Erdey et al. (*Talanta* 1962, 9, 489–493.) showed that the three hydrated oxalates lost water at three different temperatures. The TGA seems to show only one step, but the DTG clearly shows the three separate losses, one for each salt.

of the acidic sites can be estimated by chemisorption of a basic compound, such as ammonia, and then studying the desorption by TGA/DTG. As seen in Fig. 16.13, the weight change is small, about 1% total spread over two broad steps, but the two steps are clearly evident from the DTG plot.

The decomposition of polyvinyl chloride polymer (PVC) also demonstrates the power of the DTG plot. The TGA curve (solid line in Fig. 16.14) seems to show two weight loss events, but the DTG plot (dotted line in Fig. 16.14) clearly shows three steps. The loss at 280°C is due to volatilization of HCl, while the mass losses at 320°C and 460°C are due to loss of hydrocarbons. We will learn how we know this later in the chapter.

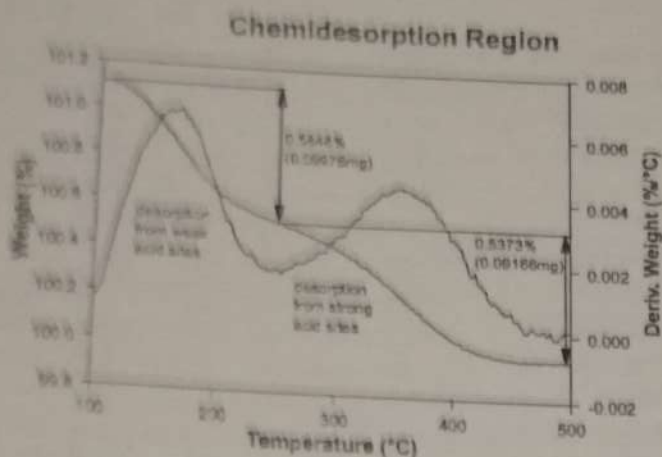


Figure 16.13 TGA and DTG thermal curves showing desorption of basic compounds from the acidic sites of a zeolite catalyst. Losses from weakly acidic sites can be distinguished from strongly acidic sites using the DTG curve, despite the fact that the overall mass loss is only about 1%. The mass scale is on the left-hand side y-axis. (Courtesy of TA Instruments, New Castle, DE, from Thermal Analysis Applications Brief TA-231.)

16.1.4. Sources of Error in Thermogravimetry

Errors in thermogravimetry can lead to inaccuracy in temperature and weight data. Proper placement of the TGA instrument in the laboratory, away from sources of vibration and heat, is essential to minimize fluctuations in the balance mechanism. Older instruments suffered from an apparent gain in weight of a sample container when heated, known as the buoyancy effect. This effect, due to the decreased buoyancy of the atmosphere,

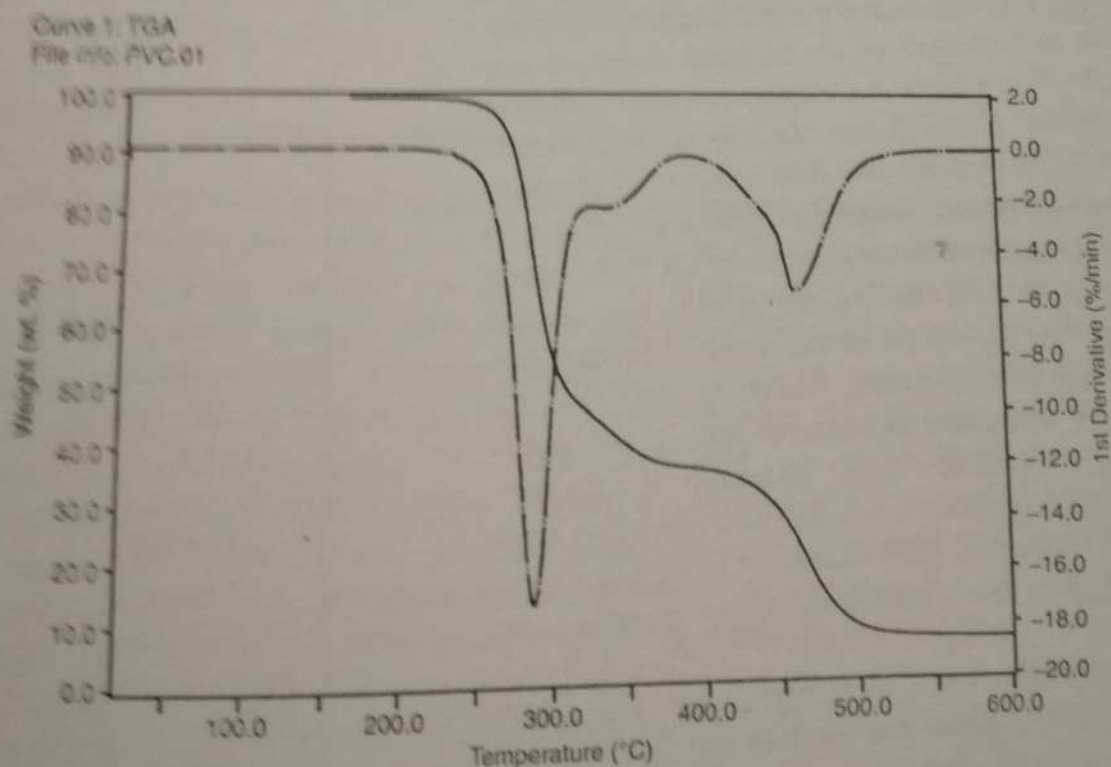


Figure 16.14 TGA (solid line) and DTG (dotted line) thermal curves of polyvinylchloride polymer heated under nitrogen. The first mass loss at 280°C is due to loss of HCl. (Courtesy of TA Instruments, New Castle, DE, from Thermal Analysis Applications Brief TA-231.)

changes in convection on heating and other complex factors, has been to a large extent eliminated in modern TGA instruments. The buoyancy effect can be evaluated and compensated for by running a blank (empty sample container) under the same conditions of heating and gas flow used for the samples. Errors can arise due to turbulence caused by the gas flow and due to convection on heating. Gas flow rates and heating rates should be kept as low as possible to minimize these effects.

Placement of the thermocouple is critical to accurate temperature measurement. Ideally, having the thermocouple in the sample itself would give the most accurate reading of the sample temperature. However, there are problems associated with putting the thermocouple into the sample. These include reaction with the sample, reproducible sample packing, sample mass, and thermal conductivity, among others. Modern instruments generally have the thermocouple in contact with the sample pan or close to the sample pan. The sample temperature is generally lower than the recorded temperature due to several factors including the finite heating rate, thermal conductivity of both the sample itself and the sample container, the gas flow rate and similar factors. There is also the heat of reaction to take into account. An endothermic reaction will cause self-cooling of a sample and therefore an even greater lag in the sample temperature than would otherwise occur, while an exothermic reaction will decrease the lag in sample temperature.

16.2. DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis (DTA) is a technique in which the difference in temperature, ΔT , between the sample and an inert reference material is measured as a function of temperature. Both sample and reference material must be heated under carefully controlled conditions. If the sample undergoes a physical change or a chemical reaction, its temperature will change while the temperature of the reference material remains the same. That is because physical changes in a material such as phase changes and chemical reactions usually involve changes in **enthalpy**, the heat content of the material. Some changes result in heat being absorbed by the sample. These types of changes are called **endothermic**. Examples of endothermic changes include phase changes such as melting (fusion), vaporization, sublimation, and some transitions between two different crystal structures for a material. Chemical reactions can be endothermic, including dehydration, decomposition, oxidation-reduction, and solid-state reactions. Other changes result in heat being given off by the sample. Such changes are termed **exothermic**. Exothermic changes include phase changes such as freezing (crystallization), some transitions between different crystal structures and chemical reactions; decomposition, oxidation-reduction, and chemisorption can be exothermic. There are also physical changes that are not simple phase changes that still cause the sample temperature to change. Examples of such physical changes include adsorption and desorption of gases from surfaces and **glass transitions** in amorphous glasses and some polymers. The glass transition is a change in an amorphous material from a brittle, vitreous state to a plastic state. Glass transitions are second order phase transitions.

DTA and the related technique of DSC to be discussed later in the chapter are capable of measuring many types of physical and chemical changes that result in enthalpy changes. It is not necessary that the sample's weight change in order to produce a DTA response. However, if a weight change does take place, as occurs on loss of water, the enthalpy of the sample invariably changes, and a DTA response will be observed. So DTA is capable of measuring the same changes measured by TGA, plus many additional changes that

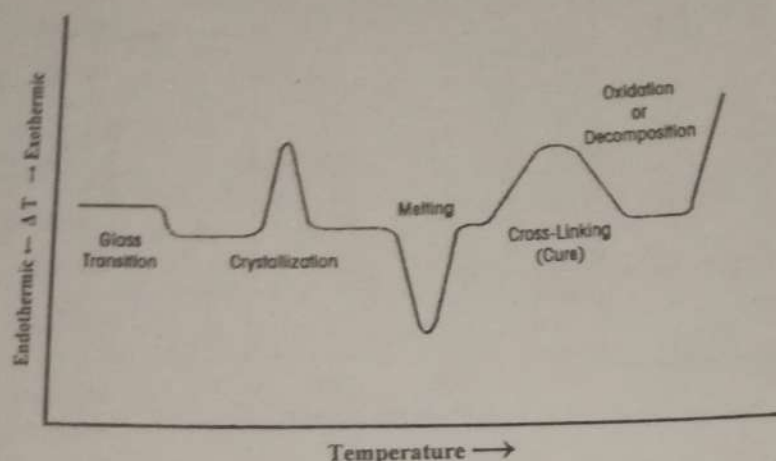


Figure 16.15 Hypothetical DTA thermal curve for a semicrystalline polymer with the ability to cross-link. The plot shows the baseline shift that occurs at the glass transition temperature, T_g , exothermic peaks for crystallization and cross-linking (or curing), an exothermic peak (offscale) for oxidative decomposition, and an endothermic peak for melting of the polymer. A similar thermal plot would be obtained by DSC analysis. (Courtesy of TA Instruments, New Castle, DE, www.tainst.com.)

TGA cannot measure because no mass change occurs. A DTA plot or thermal curve has ΔT on the y-axis and T (or time) on the x-axis, as shown schematically in Fig. 16.15. The x-axis temperature can be the temperature of the heating block, the temperature of the sample or the temperature of the reference, or it can be time. By convention, exothermic changes are plotted as positive, and the peaks point up, while endothermic changes are plotted as negative, and the peaks point down. (The same convention may be used for DSC; however, some instrument software uses the opposite convention. We will see examples of both conventions.) Some changes, such as the glass transition shown in Fig. 16.15, do not result in a peak, but only a step change in the baseline. The reason will be discussed later in the chapter.

16.2.1. DTA Instrumentation

The equipment used in DTA studies is shown schematically in Fig. 16.16. The sample is loaded into a crucible, which is then inserted into the sample well (marked S). A reference sample is made by placing a similar quantity of inert material (such as Al_2O_3) in a second crucible. This crucible is inserted in the reference well, marked R. The dimensions of the two crucibles and of the cell wells are as nearly identical as possible; furthermore, the weights of the sample and the reference should be virtually equal. The sample and reference should be matched thermally and arranged symmetrically with the furnace so that they are both heated or cooled in an identical manner. The metal block surrounding the wells acts as a heat sink. The temperature of the heat sink is slowly increased using an internal heater. The sink in turn simultaneously heats the sample and reference material. A pair of matched thermocouples is used. One pair is in contact with the sample or the sample container (as shown); the other pair is in contact with the reference. The output of the differential thermocouple, $T_s - T_r$ or ΔT , is amplified and sent to the data acquisition system. This allows the difference in temperature between the sample and

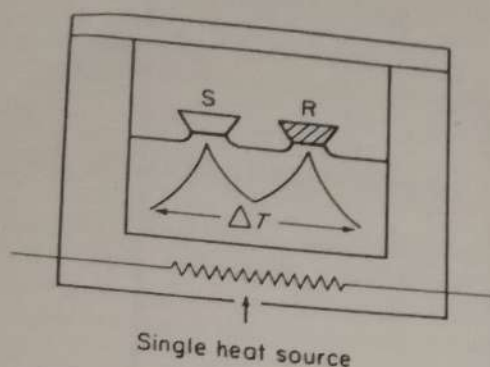


Figure 16.16 Schematic DTA instrument. (Courtesy of PerkinElmer, Inc. Shelton, CT, www.perkinelmer.com.)

the reference to be recorded as a function of either the sample temperature, the reference temperature or time. If there is no difference in temperature, no signal is generated, even though the actual temperatures of the sample and reference are both increasing. Operating temperatures for DTA instruments are generally room temperature to about 1600°C , although one manufacturer makes a DTA capable of operating from -150°C to 2400°C . To reach the very low subambient temperatures, a liquid nitrogen cooling accessory is needed. Some low temperatures (but not -150°C) may be reached with electrical cooling devices or with forced air-cooling.

When a physical change takes place in the sample, heat is absorbed or generated. For example, when a metal carbonate decomposes, CO_2 is evolved. This is an endothermic reaction; heat is absorbed and the sample temperature decreases. The sample is now at a lower temperature than the reference. The temperature difference between the sample and reference generates a net signal, which is recorded. A typical example of a DTA thermal curve is shown in Fig. 16.15. If, in the course of heating, the sample undergoes a phase transition or a reaction that results in the generation of heat, that is, an exothermic reaction, the sample becomes hotter than the reference material. In this case, the sample heats up to a temperature higher than that of the reference material until the reaction is completed. The sample then cools down or the temperature of the reference cell catches up until its temperature and that of the heat cell once again become equal. Such an effect is shown on the thermal curve as a peak that moves in a positive (upward) direction rather than in the negative direction, which allows us to distinguish between exothermic and endothermic reactions. The DTA experiment is performed under conditions of constant pressure (usually atmospheric pressure). Under constant pressure, the change in heat content of a sample (the change in *enthalpy*) is equal to the heat of reaction, ΔH . Any chemical or physical change that results in a change in ΔH gives a peak in the DTA thermal curve. There are some types of changes that do not result in a peak in the thermal curve but only a change in the baseline, as shown schematically in Fig. 16.15. These types of changes do not undergo a change in ΔH , but a change in their *heat capacity*, C_p . Heat capacity is sometimes referred to as specific heat, and is the amount of heat required to raise the temperature of a given amount of material by 1 K. If the amount of material is specified to be 1 mole, the heat capacity is therefore the molar heat capacity, with units of J/mol K . The most common process that gives rise to a change in baseline but not a peak in the DTA is a "glass transition" in materials such as polymers or glasses. The glass transition is discussed briefly under applications of DTA.

Modern DTA instruments have the ability to change atmospheres from inert to reactive gases, as is done in TGA. As is the case with TGA, the appearance of the DTA thermal curve depends on the particle size of the sample, sample packing, the heating rate, flow characteristics inside the furnace, and other factors. Thermal matching between the sample and the reference is often improved by diluting the sample with the inert reference, keeping the total masses in each crucible as close to each other as possible.

The peak area in a DTA thermal curve is related to the enthalpy change for the process generating the peak, so DTA instruments must be calibrated for both temperature and for peak area. The National Institute for Standards and Technology (NIST), a US government agency, has certified high purity metals like indium, tin, and lead with melting points known to six significant figures and enthalpies known to three or four significant figures, and a series of high purity salts with solid state transition enthalpies which are accurately known. These materials can be used to calibrate both temperature and peak area.

Sample crucibles are generally metallic (Al, Pt) or ceramic (silica) and may or may not have a lid. Many metal pans with lids have the lid crimped on using a special tool. Best results are obtained when the area of contact between the sample and the pan or crucible is maximized. Samples are generally in the 1–10 mg range for analytical applications.

The peak area in DTA is related to the enthalpy change, ΔH , to the mass of sample used, m , and to a large number of factors like sample geometry and thermal conductivity. These other factors result in the area, A , being related to the mass and ΔH by an empirically determined calibration constant, K :

$$A = K(m)(\Delta H) \quad (16.1)$$

Unfortunately, K is highly temperature-dependent in the DTA experiment, so it is necessary to calibrate the peak area in the same temperature region as the peak of interest. This may require multiple calibration standards and can be time consuming. As we shall see, the calibration constant K for DSC is not temperature dependent; therefore DTA is usually used for qualitative analysis, while DSC is used for quantitative measurements of ΔH and heat capacity.

16.2.2. Analytical Applications of DTA

DTA is based on changes of heat flow into the sample. Using DTA, we can detect the decomposition or volatilization of the sample, just as we can with TGA. In addition, however, physical changes that do not involve weight changes can be detected by DTA. Such changes include crystallization, melting, changes in solid crystal phases, and homogeneous reactions in the solid state. In each of these changes there is a flow of heat between the sample and its surroundings caused by endothermic or exothermic transitions or by changes in the heat capacity. The main use of DTA is to detect thermal processes and characterize them as exothermic or endothermic, reversible or irreversible, but only qualitatively. DTA thermal curves can be used to determine the order of a reaction (kinetics), and can provide the information required to construct phase diagrams for materials. DTA can be used for characterization of engineering materials, for the determination of the structural and chemical changes occurring during sintering, fusing, and heat treatments of alloys to change microstructure, identification of different types of synthetic rubbers, and determination of structural changes in polymers.

An instance of the use of transitions where no change in weight occurs is the DTA characterization of polymers. The physical properties, such as strength, flexibility, and solubility, of a polymer depend (among other things) on its degree of crystallinity. Crystalline materials are those materials that exhibit a high degree of long-range and short-range

order in the arrangement of their molecules or atoms. No polymers are 100% crystalline, but some polymers can partially crystallize; these are called **semicrystalline** polymers. A polymer is a gigantic organic molecule, or **macromolecule**, with a high molecular weight, typically 5000–40,000 g/mol. Polymer molecules generally exist as long and flexible chains. The chains are capable of bending and twisting, as shown in Fig. 16.17(a). A bulk polymer consists of large numbers of these chains, all intertwined like a bowl of cooked spaghetti noodles or rumpled pieces of string. A polymer in this state, with no short-range or long-range order, is said to be **amorphous**. With some types of polymers and proper treatment, such as slow cooling from the molten state, some of these long chains can form crystalline zones that are regularly oriented [Fig. 16.17(b)]. The DTA curves of the two samples in Fig. 16.17 would appear as in Fig. 16.18 for samples that had been rapidly cooled (quenched) from the liquid state. At the glass transition temperature, T_g , a polymer goes from a glassy, rigid state to a rubbery state as the temperature now permits large-scale molecular motion. At the glass transition, there is a change in the heat capacity, C_p , of the polymer, which is seen as a step-change in the baseline of the thermal curve. There is no change in the enthalpy at T_g , so no peak occurs in the thermal curve. There is also a change in the rate of volume expansion of the polymer at T_g , which can be measured by thermomechanical analysis, TMA. On further heating, crystallization of the semicrystalline polymer occurs as the viscosity drops, molecular mobility increases, and the chains align themselves into ordered regions, resulting in an exothermic peak. The amorphous polymer shows no such exothermic peak. Additional heating will generally result in the melting of semicrystalline polymer, seen as an endothermic peak in the thermal curve. None of these transitions involves a change in mass of the sample, so none of these changes would be seen in a TGA thermal curve. Amorphous polymers do not melt, but may show an endothermic decomposition peak on continued heating. This decomposition would be seen by both DTA and TGA, since decomposition does involve weight loss. The degree of crystallinity in the semicrystalline polymer can be calculated from the heat of fusion (the area under the crystallization exotherm), but quantitative measurements of this sort are usually performed by DSC because DSC is more accurate than DTA for quantitative analysis.

Qualitative identification of materials is done by comparing the DTA of the sample to DTA thermal curves of known materials. DTA thermal curves serve as fingerprints for materials.

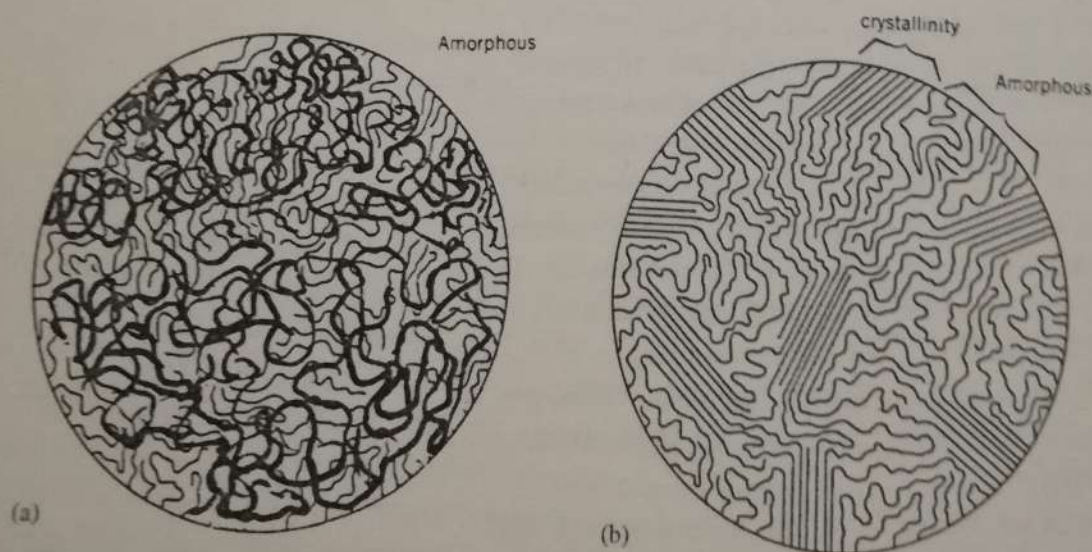


Figure 16.17 (a) Amorphous polymer structure (b) semicrystalline polymer structure with aligned chains in the crystalline regions and random structure in the amorphous region.

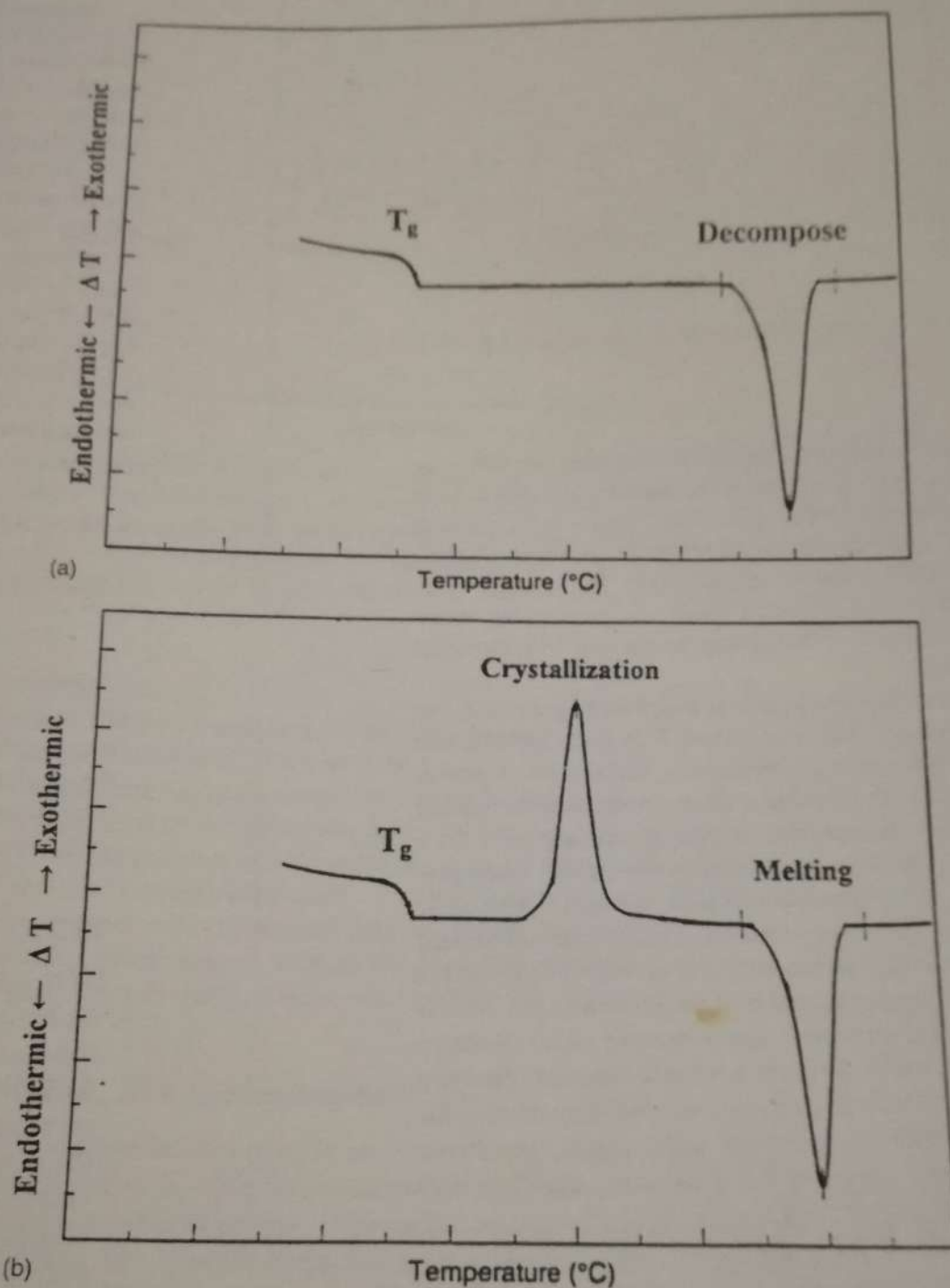


Figure 16.18 Schematic DTA thermal curves for the totally amorphous polymer structure and the semicrystalline polymer structure shown in Fig. 16.17. Both show T_g ; only the semicrystalline polymer has a crystallization exotherm.

Theoretically, the area under each DTA peak should be proportional to the enthalpy change for the process that gave rise to the peak. Unfortunately, in a traditional simple DTA, there are many factors that are not compensated for. For example, DTA response generally decreases as the temperature increases. This makes the area under the peaks unreliable for enthalpy measurements unless the DTA has been calibrated in the

temperature range of interest. Semiquantitative results for enthalpies can be obtained, but for quantitative enthalpy measurements, we turn to the DSC.

16.3. DIFFERENTIAL SCANNING CALORIMETRY

In DSC, differences in heat flow into a reference and sample are measured vs. the temperature of the sample. The difference in heat flow is a difference in energy; DSC is a calorimetric technique, and results in more accurate measurement of changes in enthalpy and heat capacity than that obtained by DTA.

16.3.1. DSC Instrumentation

The DSC measurement requires a sample and a reference, as does DTA. Modern DSC sample and reference pans are small and usually made of aluminum. They may or may not have lids. Sample size is generally 1–10 mg. Often the reference pan is left empty, but an inert reference material such as is used in DTA may be used. Commercial DSC equipment can operate at temperatures from -180°C to 700°C , with specialized instruments capable of maximum temperatures of 1600°C . The DSC must be able to be heated and cooled in a controlled manner. To achieve the very low end of the temperature range, a special liquid nitrogen cooling accessory is needed; for other cooling applications, electrical cooling or forced air cooling is used. Modern DSC instruments are available with automatic intelligent sample changers that permit the unattended analysis of as many as 50 samples or more in any order specified by the analyst.

There are two main types of DSC instrumentation, heat flux DSC and power compensated DSC. A schematic of a commercial **heat flux DSC** is presented in Fig. 16.19. In a heat flux instrument, the same furnace heats both the sample and the reference. In heat flux DSC, the temperature is changed in a linear manner while the differential heat flow into the sample and reference is measured. The sample and reference pans sit on the heated thermoelectric disk, made of a Cu/Ni alloy (constantan). The differential heat flow to the sample and reference is monitored by area thermocouples attached to the bottom of the sample and reference positions on the thermoelectric disk. The differential heat flow into the pans is directly proportional to the difference in the thermocouple signals. The sample temperature is measured by the alumel/chromel thermocouple under the sample position. This temperature is an estimated sample temperature because the thermocouple is not inserted into the sample itself. The accuracy of this temperature will depend on the thermal conductivity of the sample and its container, the heating rate, and other factors. As shown in Fig. 16.19, the sample and reference pans both have lids and the reference pan is an empty pan. A schematic of a **power compensated DSC** is presented in Fig. 16.20. The major difference in power compensated DSC instruments is that two separate heating elements are used for the sample (marked P in Fig. 16.20) and the reference. A change in temperature between the sample and the reference serves as the signal to "turn on" one of the heaters so that the sample and the reference stay at the same temperature. When a phase change, reaction, glass transition, or similar event occurs in the sample, the sample and reference temperatures become different. This causes extra power to be directed to the cell at the lower temperature in order to heat it. In this manner, the temperatures of the reference and sample cells are kept virtually equal ($\Delta T = 0$) throughout the experiment. The power and temperature are measured accurately and continuously. The temperatures of the sample and reference are measured using Pt resistance sensors, shown in Fig. 16.20. The difference in power input is plotted vs. the average temperature

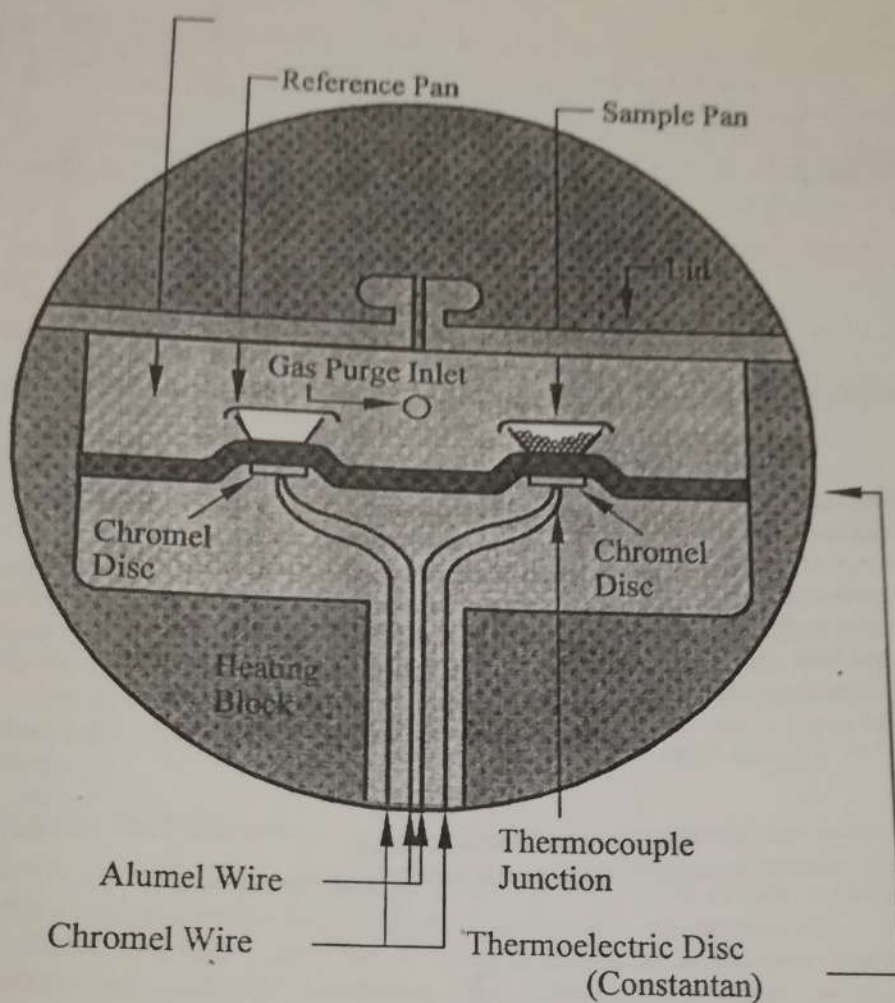


Figure 16.19 Schematic of a heat-flux DSC. (Courtesy of TA Instruments, New Castle, DE, www.tainst.com.)

of the sample and reference. Power compensation provides high calorimetric accuracy, high precision, and high sensitivity. This permits analysis of very small samples as demonstrated in Fig. 16.21, showing the determination of the heat of fusion of a 6 μg sample of indium metal. Note that this figure is plotted opposite to the convention normally used for endothermic peaks.

The DSC peak area must be calibrated for enthalpy measurements. The same types of high purity metals and salts from NIST discussed for calibration of DTA equipment are also used to calibrate DSC instruments. As an example, NIST SRM 2232 is a 1 g piece of high purity indium metal for calibration of DSC and DTA equipment. The indium SRM is certified to have a temperature of fusion equal to $156.5985^\circ\text{C} \pm 0.00034^\circ\text{C}$ and a certified enthalpy of fusion equal to $28.51 \pm 0.19 \text{ J/g}$. NIST offers a range of similar standards. These materials and their certified values can be found on the NIST website at www.nist.gov. Government standards organizations in other countries offer similar reference materials.

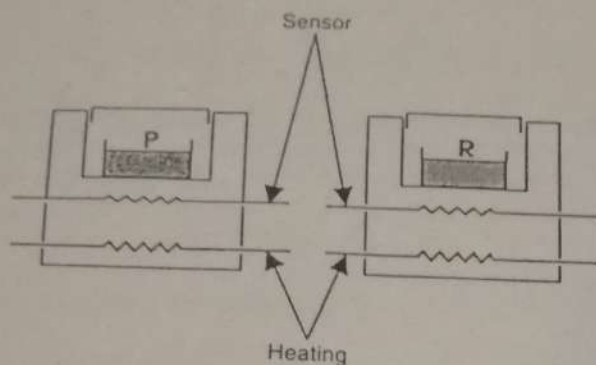


Figure 16.20 Schematic of a power-compensated DSC. (Courtesy of PerkinElmer, Inc. Shelton, CT, www.perkinelmer.com.)

The resultant thermal curve is similar in appearance to a DTA thermal curve, but the peak areas are accurate measures of the enthalpy changes. Differences in heat capacity can also be accurately measured and are observed as shifts in the baseline before and after an endothermic or exothermic event or as isolated baseline shifts due to a glass transition. Because DSC provides accurate quantitative analytical results, it is now the most used of the thermal analysis techniques. A typical DSC thermal curve for polyethylene terephthalate, the polymer used in many soft drink bottles, is shown in Fig. 16.22.

16.3.2. Applications of DSC

DSC is used to study all of the types of reactions and transitions that can be studied using DTA, with the added advantage of accurate quantitative measurements of ΔH and ΔC_p .

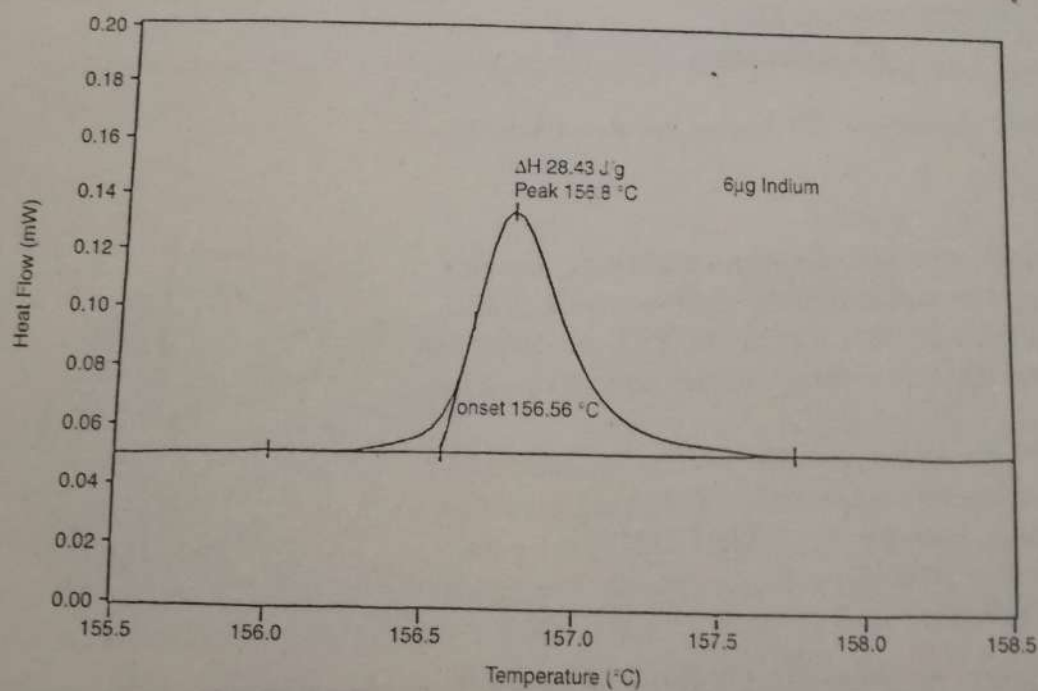


Figure 16.21 DSC thermal curve showing the determination of the enthalpy of vaporization of 6 µg of indium metal. (Courtesy of PerkinElmer, Inc. Shelton, CT, www.perkinelmer.com.)

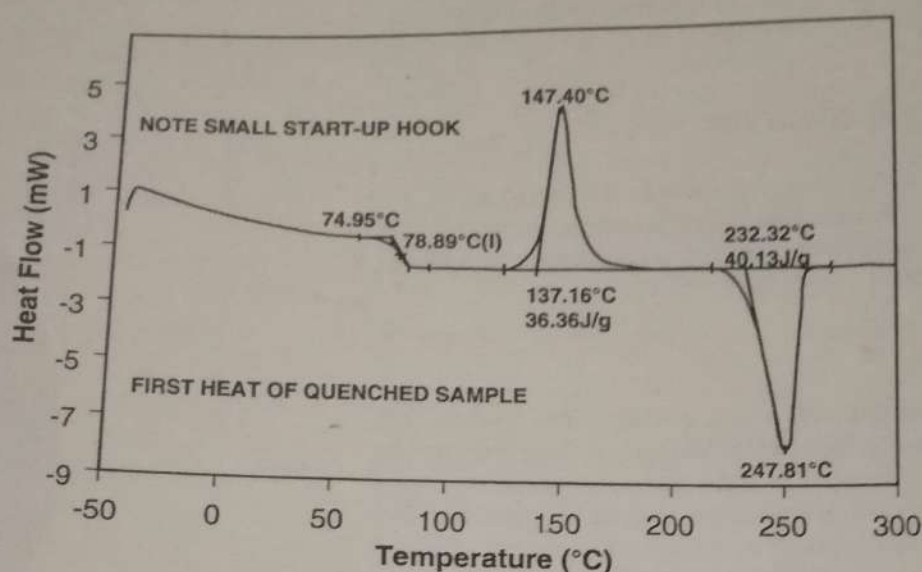


Figure 16.22 DSC thermal curve for a sample of polyethylene terephthalate (PET). T_g is observed at 78.9°C. Crystallization begins at 137°C and the area under the exothermic peak is equivalent to 36.36 J/g PET. Melting begins at about 323°C; the area under the endothermic peak is equivalent to 40.13 J/g PET. (Courtesy of TA Instruments, New Castle, DE, www.tainst.com.)

Polymer chemists use DSC extensively to study percent crystallinity, crystallization rate, polymerization reaction kinetics, polymer degradation, and the effect of composition on the glass transition temperature, heat capacity determinations, and characterization of polymer blends. Materials scientists, physical chemists, and analytical chemists use DSC to study corrosion, oxidation, reduction, phase changes, catalysts, surface reactions, chemical adsorption and desorption (chemisorption), physical adsorption and desorption (physisorption), fundamental physical properties such as enthalpy, boiling point, and equilibrium vapor pressure. DSC instruments permit the purge gas to be changed automatically, so sample interactions with reactive gas atmospheres can be studied.

For example, from Fig. 16.22, the heat of crystallization is measured to be 36.36 J/g and the heat of melting (or fusion) is measured to be 40.13 J/g by integration of the respective peaks by the instrument data analysis software. For this polymer sample, the measured heat of crystallization is slightly lower than the measured heat of melting, indicating that the polymer was partly crystalline at the start of the experiment. The T_g and the specific heat can also be accurately measured from this thermal curve.

The heat of fusion is a useful measure of the percent crystallinity of polymers. Table 16.3 presents heat of fusion data and the calculated percent crystallinity for three

Table 16.3 DSC Results for Three Samples of Polyethylene

Sample	Melt onset (°C)	Melt peak (°C)	Enthalpy (J/g)	%crystallinity
1	121.9	132.9	195.9	67.6
2	121.3	132.6	194.5	67.1
3	122.3	131.6	180.1	62.1

Source: From TA Instruments Applications Brief TA-123, courtesy of TA Instruments, Inc., New Castle, DE, USA.

different samples of polyethylene. The percent crystallinity is calculated from calibration with either a 100% crystalline sample or a sample of known crystallinity. The first two samples in the table are identical in percent crystallinity and in their melting behavior; the third sample, however, has a lower percent crystallinity and a sharper melting profile (compare the melt onset and melt peak temperature columns). This tells the polymer chemist that sample 3 has been processed differently and will have different physical and mechanical properties than samples 1 and 2. The sharp melting of sample 3 is shown in Fig. 16.23.

16.3.2.1. Pressure DSC

Normally, DSC experiments are run at atmospheric pressure. Running samples under different pressures can extend the usefulness of DSC. DSC instruments are available with high-pressure cells capable of operating at up to 1000 psi (47 kPa). Changing the pressure will affect any reactions involving gases, while not having any significant effect on condensed phases. Boiling is the phase change of a material from liquid to gas. The boiling point of a material increases as the pressure increases, while the melting point (a phase change involving only solid and liquid) does not change significantly with pressure. Therefore, changing the pressure facilitates interpretation of peaks in a DSC thermal curve. If the peak shifts in temperature as a function of pressure, a gas is involved in the reaction that gave rise to the peak. Because the pressure affects the boiling point of a liquid, a series of experiments in a pressure DSC cell at known pressures yields boiling point shifts. These shifts can be used to obtain quantitative vapor pressure information on liquids.

Increasing the pressure will often increase the rate of a reaction involving gases. Adsorption of hydrogen is often used as a means of characterizing precious metal catalysts, such as the platinum catalysts used in automobile catalytic converters and the Pt and Pd catalysts used in large-scale organic chemical synthesis. A typical adsorption study may require large samples and take 6 h or more. The same type of study can be run in a pressure DSC cell in ~15 min. The high pressure of hydrogen accelerates the reaction. The adsorption and

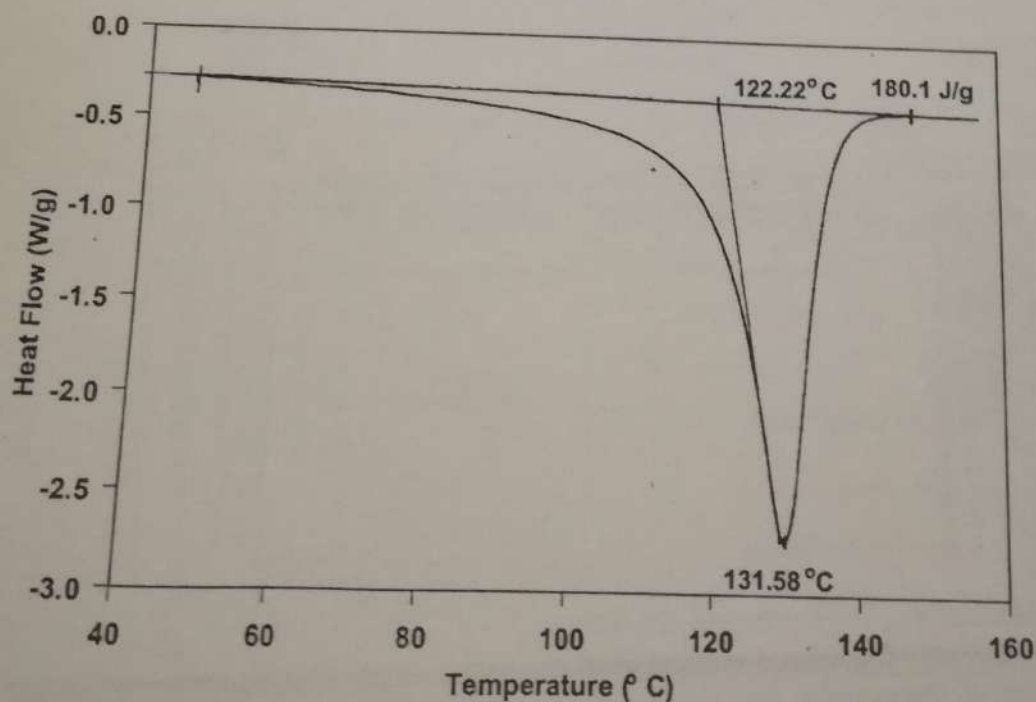


Figure 16.23 Melting point of a polyethylene sample by DSC. (Courtesy of TA Instruments, New Castle, DE. From Thermal Analysis Applications Brief TA-123.)

desorption of hydrogen on palladium as studied by DSC is shown in Fig. 16.24. Many sample-atmosphere reactions such as oxidation of oils and greases can be accelerated by increasing the pressure of air or oxygen and can also be studied effectively by pressure DSC. Other pressure sensitive reactions, such as volatilization, are slowed down by increased pressure. Suppression of these reactions can be a valuable tool when pressure DSC is used to study a complex system.

16.4. HYPHENATED TECHNIQUES

16.4.1. Hyphenated Thermal Methods

While TGA provides useful data when a mass change is involved in a reaction, we have seen that many reactions do not have a change in mass associated with them. The use of both TGA and DTA or TGA and DSC provides much more information about a sample than either technique alone provides. There are several commercial thermal analysis instrument manufacturers who offer simultaneous combination systems. Simultaneous TGA-DTA and simultaneous TGA-DSC instruments are available. Instrument combinations cover a wide temperature range and come in both "analytical sample" size (1–20 mg) and high-capacity sample size. A schematic of a simultaneous TGA-DTA instrument is presented in Fig. 16.25, showing the dual sample and reference pans. The instrument monitors both the weight change and the temperature difference between the sample and reference, and plots both the TGA and DTA thermal curves simultaneously. A hypothetical sample might have plots like those in Fig. 16.26, where two of the DTA peaks are clearly associated with the mass losses in the TGA, and there are two other "events" with enthalpy changes but no mass changes.

16.4.2. Evolved Gas Analysis

The evolution of gas from a thermal analyzer such as a TGA, DTA, or DSC may be determined using *evolved gas detection* (EGD) or, if qualitative or quantitative analysis of the gas is required, *evolved gas analysis* (EGA). These techniques are essentially a combination of thermal analysis and MS, tandem mass spectrometry (MS-MS), GC-MS or other

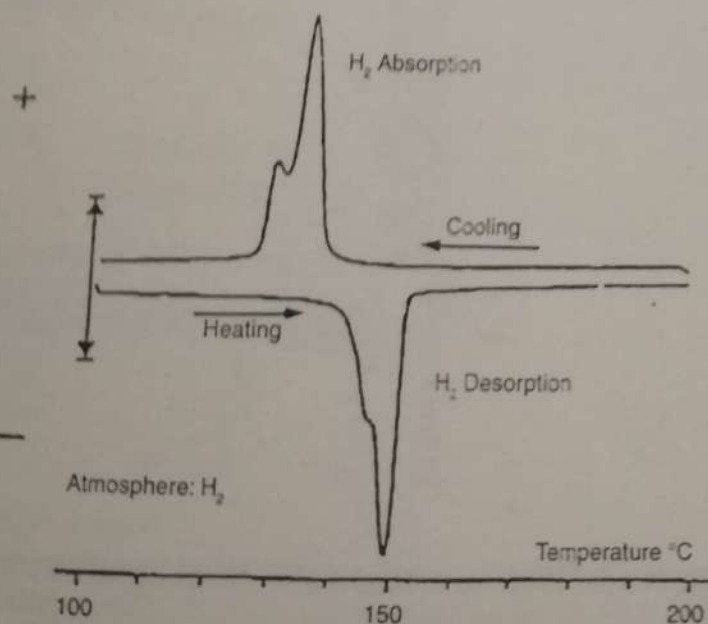


Figure 16.24 DSC thermal curve of adsorption and desorption of hydrogen from a precious metal catalyst under constant pressure.

TG/DTA Schematic

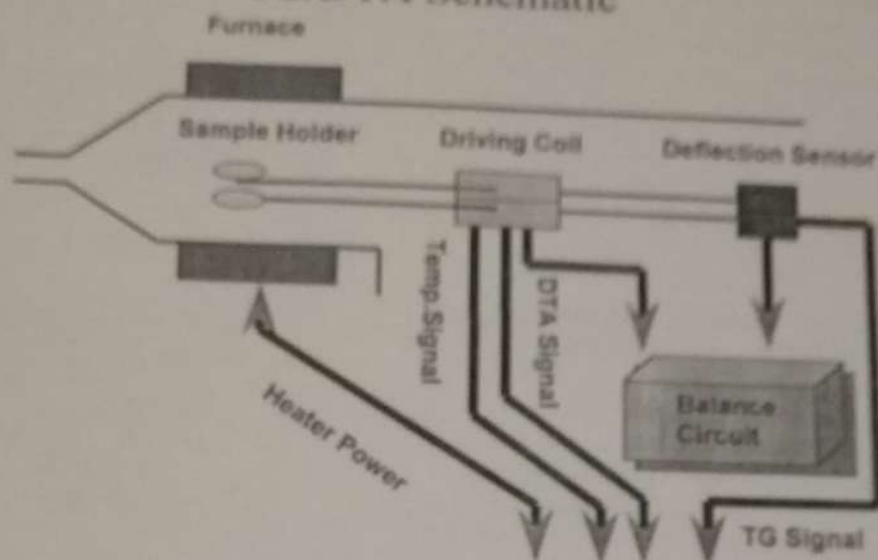


Figure 16.25 A schematic simultaneous TGA-DTA instrument. A weight change on the sample side displaces the beam and a drive coil current returns the beam to zero. The current is proportional to the weight change and serves as the TGA signal. The temperature change between the sample and reference pans is measured by thermocouples attached to the pans. The temperature differential is the DTA signal. (Courtesy of ThermoHaake, Inc., Paramus, NJ, www.thermo.com, and Seiko Instruments, Japan.)

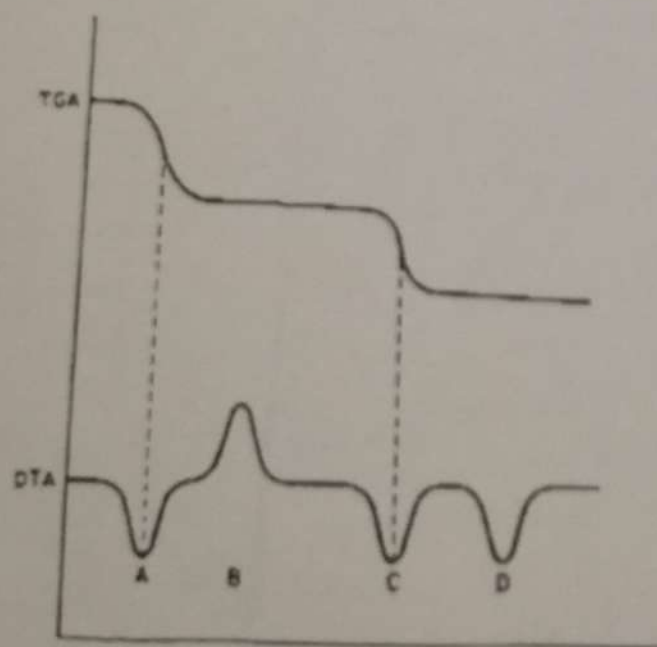
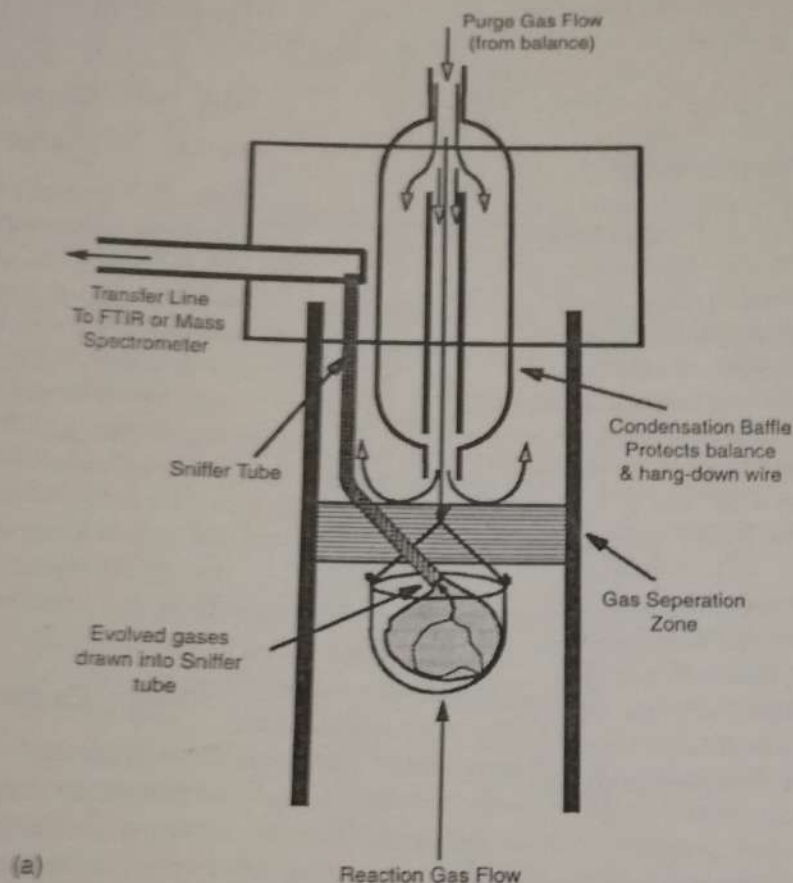


Figure 16.26 The TGA and DTA curves of a hypothetical sample. The two steps in the TGA curve result from weight losses. They correspond to the endothermic peaks A and C in the DTA plot. The DTA thermal curve also shows an exothermic event, B, and an endothermic event, D, that do not involve a change in mass.

species-selective detectors, such as FTIR. The evolved gases from the furnace are carried through a heated transfer line to the mass spectrometer or FTIR or other gas analyzer. This permits real-time identification of the gases given off by the sample during the thermal program. Figure 16.27(a) presents a commercial interface for capturing the



Synergy System — TGA-FTIR/MS/GC

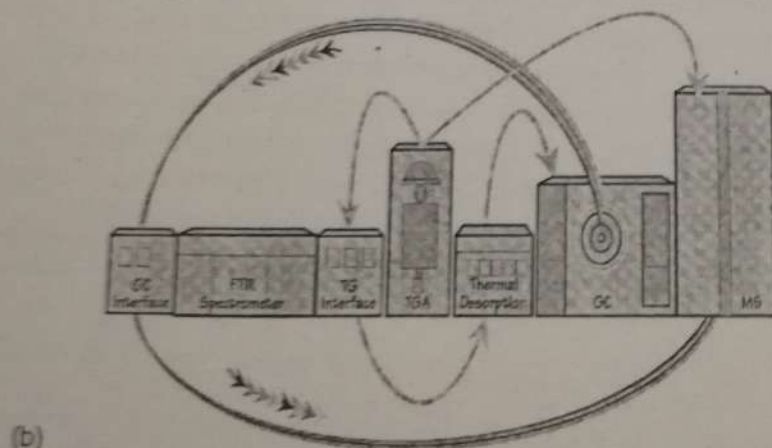


Figure 16.27 (a) The Sniffer[®] interface for evolved gas analysis. The Sniffer tube sits directly above the sample pan and draws evolved gases to both an FTIR and a GC-MS with minimal dilution. The interface is shown in a high-capacity TGA. (Courtesy of ThermoCahn, Madison, WI, www.thermo.com.) (b) The high-capacity TGA with Sniffer coupled simultaneously to an FTIR spectrometer and a GC-MS system. (Courtesy of ThermoCahn, Madison, WI, www.thermo.com.)

evolved gases from a TGA and sending evolved gas to both an FTIR and a GC-MS simultaneously [Fig. 16.27(b)]. This particular interface is used with a high-capacity TGA (up to 100 g sample size), so whole electronic components and fabricated parts can be analyzed. This can make failure analysis and production control very simple.

The alternative to real-time detection is to have a system for trapping the evolved gases and storing the trapped gases for analysis at a later time. Sorbents for collecting the evolved gases can be liquid or solid. The sorbents can be selective for a specific gas or a class of gaseous compounds. If no adsorbent material is desired, cryogenic trapping may be used.

The two most common instruments interfaced to thermal analyzers are FTIR instruments, discussed in Chapter 4 and MS instruments, discussed in Chapters 9 and 10. FTIR is less sensitive and less versatile than MS, but is simpler and cheaper. For hyphenated thermal analysis-FTIR, a heated transfer line from the thermal analyzer is connected to a heated FTIR gas cell, as shown in Fig. 16.28. The interface is relatively simple, because FTIR normally operates at ambient pressure as does the thermal analyzer. IR spectra are simple to interpret and reference libraries of gas phase IR spectra are available for the common gases and volatile organic compounds. This makes positive identification of the evolved gas straightforward if the gas is one of the gases that often accompany the decomposition of a material, such as water vapor, CO, or HCl, for example. The decomposition of PVC polymer can be studied by TGA-FTIR. Looking back at Fig. 16.14, we have the TGA thermal curve for PVC heated in nitrogen atmosphere. If the TGA is connected to an FTIR, the spectrum corresponding to the gas evolved at the first mass loss is the gas phase spectrum of HCl, Fig. 16.29, indicating that the first step in the decomposition of PVC in an inert atmosphere is loss of HCl from the polymer.

MS has more analytical flexibility than FTIR, but interfacing a thermal analyzer is difficult because of the low operating pressure required for MS. MS instruments typically operate at approximately 10^{-5} torr, while thermal analyzers are usually at atmospheric pressure. One approach is to evacuate the thermal analyzer, but the common method

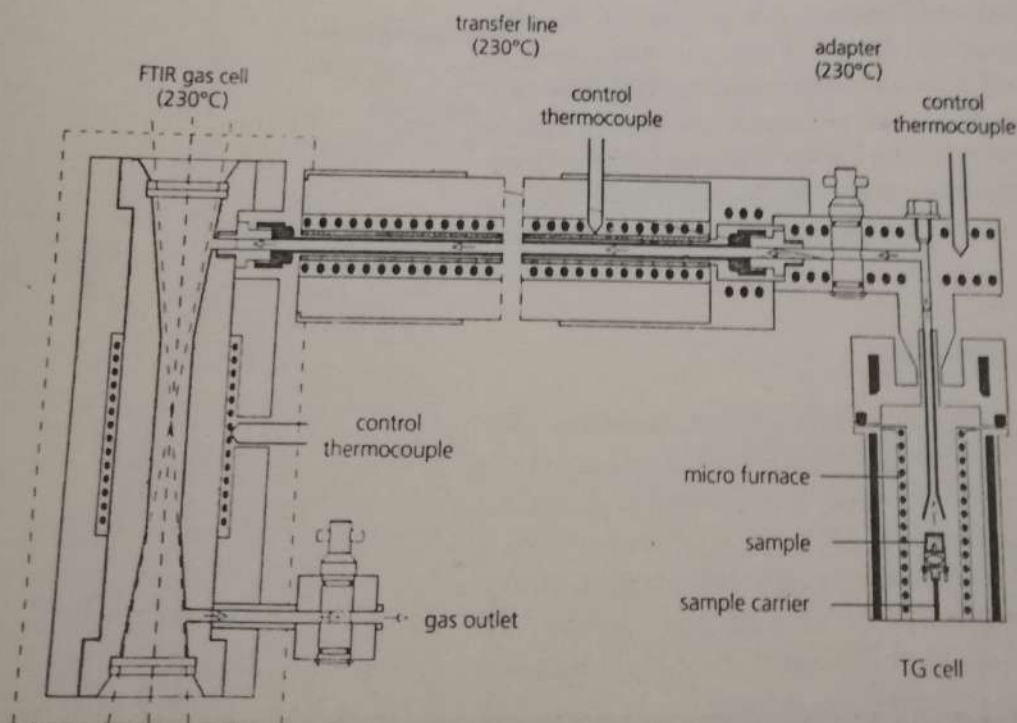


Figure 16.28 Hyphenated TGA-FTIR, showing the heated transfer line and heated IR gas cell. (Courtesy of Netzsch Instruments, Inc., Paoli, PA.)

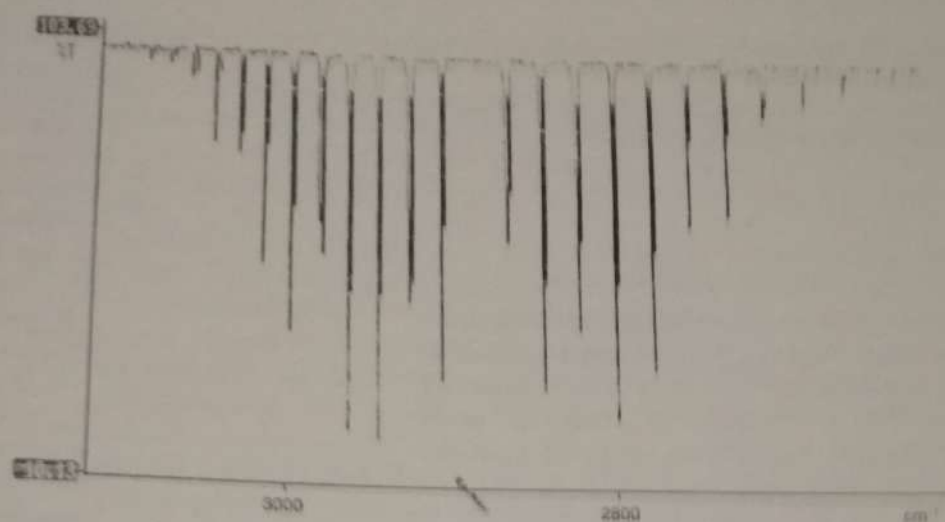


Figure 16.29 Gas phase FTIR spectrum of HCl. Spectrum collected on a PerkinElmer Paragon 1000 FTIR by Mr. Mark Bielaska, Rensselaer Polytechnic Institute, Troy, NY. Used with permission.

used is a differential pumping system such as that used for GC-MS. This reduces the pressure from the thermal analyzer in several stages prior to allowing the gas flow into the mass analyzer. A commercial interface for a thermal analyzer-MS system, shown in Fig. 16.30, uses a supersonic jet to skim analyte molecules into the MS, in a manner

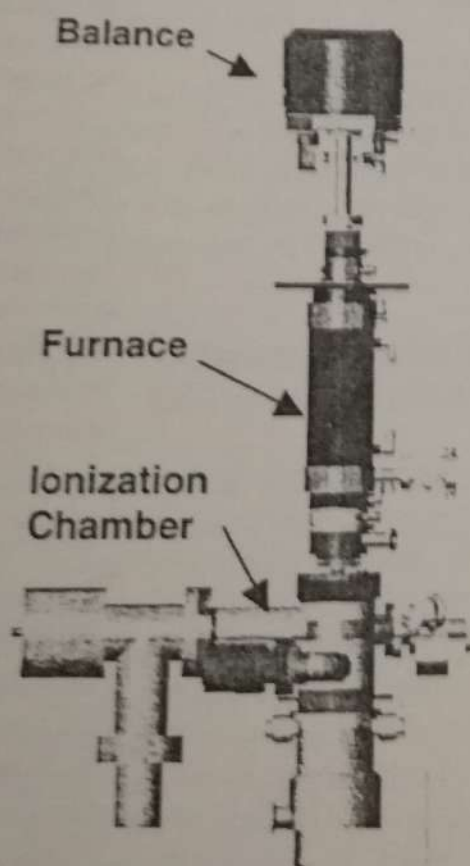


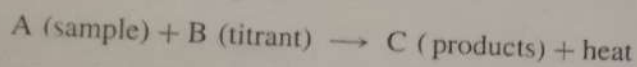
Figure 16.30 Commercial "supersonic" interface between a thermal analyzer and a mass spectrometer. The mass spectrum of evolved gases (up to molecular weights of 1024 Da) can be obtained to provide identification of the structure with no condensation during transfer between the thermal analyzer and the mass spectrometer. (Courtesy of Setaram, SA, Caluire, France.)

similar to the jet separators used in GC-MS. Jet separator operation is discussed in the chapter on GC (Chapter 12) under hyphenated techniques.

Evolved gas analysis is used for materials characterization, polymer analysis, characterization of oil shale, oxidation and reduction studies, evaluation of catalysts, and many other applications.

16.5. THERMOMETRIC TITRIMETRY

Thermometric titration depends on measuring the heat generated during a chemical reaction; therefore it is another **calorimetric technique**. Usually the reactions take place at room temperature under conditions such that no heat enters or leaves the titration cell except that brought in by introduction of the titrant. In this procedure a titrant of known concentration is added to a known volume of sample. The titration reaction follows the generalized chemical equation



For any particular reaction, a mole of A titrated with a mole of B will generate a fixed quantity of heat, which is the heat of reaction. If there is half a mole of A present, half as much heat is generated, even if there is an excess of B. Heat is generated only while A and B react with each other; an excess of either one does not cause generation of heat. The reaction is usually set up in an insulated beaker, a Dewar flask, or a Christiansen adiabatic cell. This ensures a minimum of heat loss from the system during titration.

In practice, the temperature of the system is measured as the titrant is added to the sample. A thermometric titration plot generally has ΔT on the y-axis and volume of titrant on the x-axis. A typical plot for an exothermic reaction is shown in Fig. 16.31. We will

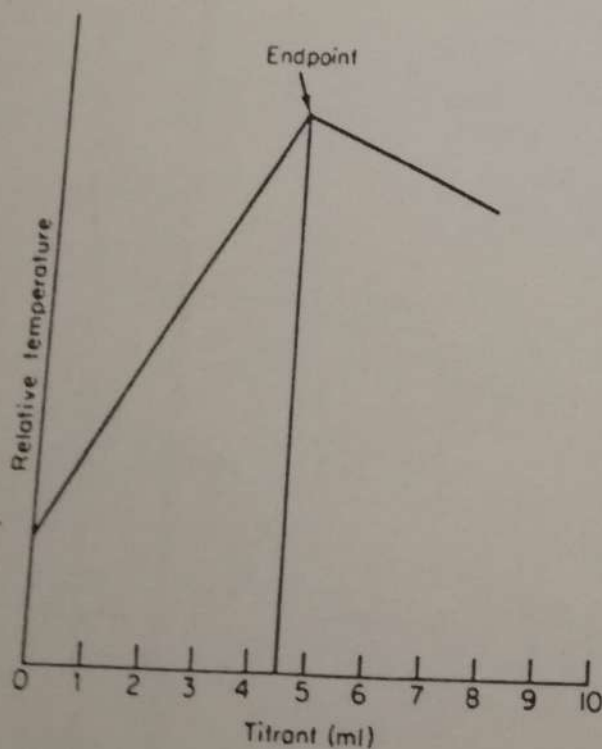


Figure 16.31 Representative thermometric titration plot. The endpoint is denoted by an abrupt change in the slope of the curve. The thermometric titration plot for HCl (a strong acid) with NaOH would look virtually identical to the thermometric titration plot for boric acid (a very weak acid) with NaOH because the ΔH of reaction is almost the same for both acids.

assume that the sample solution and the titrant are initially at room temperature. As titrant is added and the exothermic reaction occurs, the temperature of the solution increases. It can be seen that the temperature of the mixture increases until approximately 4.5 ml. of titrant have been added to the sample. This is the equivalence point of the titration. Further addition of titrant causes no further reaction, because the entire sample A has been consumed. The temperature of the mixture steadily decreases as the cooler titrant is added to the warm mixture. The endpoint can therefore be determined as the abrupt change in slope that occurs at the equivalence point. In these circumstances it is not necessary to add exactly the stoichiometric amount of titrant. Any excess added does not result in an increase in temperature, and is therefore not a source of error as it is in conventional volumetric analysis.

For simple titrations the equipment necessary is not particularly sophisticated; a thermometer, a buret, and an insulated beaker (or even two Styrofoam cups, one sitting in the other) will do. However, if one wants to measure specific heats or the heat of reaction, better control is required. Modern automated thermometric titrators consist of a constant delivery pump for the titrant, a temperature control system for the titrant, an insulated cell, calibration circuitry, electronic temperature sensing, and a data processing system. Most modern instruments are totally computerized, so different methods can be programmed and run unattended.

The titrant is delivered with a motorized syringe pump. This permits the volume of titrant to be calculated from the rate of delivery. These pumps are able to deliver rates of flow down to microliters per minute with high precision. The temperature control system, usually a thermostatted bath for the titrant and a heater for the sample cell, is used to bring the titrant and the sample to exactly the same temperature. This is required for high precision measurements of heat capacity and enthalpy. Modern thermostats can maintain the temperature to within 0.001°C .

For precise measurements of reaction parameters such as rate constants, equilibrium constants, and enthalpies, a well-designed insulated titration cell is required. The cell should have minimum heat loss to the surroundings. It should have as small a mass as possible to minimize the contribution of the cell to the total heat capacity and to maximize the response of the system to temperature changes. The calibration circuitry is used to determine the heat capacity of the system, which must be known if accurate heats of reaction are to be measured. Thermistors, which are temperature-sensitive semiconductors, are used as the temperature sensors in these systems due to their small size, fast response, and sensitivity.

16.5.1. Applications of Thermometric Titrimetry

A major use of thermometric titrimetry is for the titration of very weak acids or bases. The pH for the titration of a weak acid with a strong base (or vice versa) is easily calculated and such calculations can be found in standard analytical chemistry texts. Strong acids such as HCl, when titrated with strong base, give a large change in pH as the equivalence point is reached; therefore the quantitative determination of a strong acid using a potentiometric titration with a glass pH electrode is very simple. As the acid becomes weaker, the change in pH near the equivalence point decreases until the equivalence point becomes too shallow to detect by potentiometric titration. For example, the weak acid boric acid, with $\text{p}K_1 = 9.24$ and $\text{p}K_2 = 12.7$, does not give a good end point in a potentiometric titration with NaOH because the inflection is too small. However, in a thermometric titration with NaOH, boric acid gives a sharply defined end point, and is easily determined, because the ΔH for the boric acid neutralization is large. It is very similar in magnitude to that

for neutralization of HCl by NaOH. Thermometric titrations can be used for quantitative analysis using neutralization reactions, oxidation-reduction reactions, and complexation reactions, as well as to determine heats of mixing and to determine equilibrium constants.

In thermometric titration it is assumed that the rate of reaction is relatively fast and that the endpoint will occur as soon as a small excess of titrant is added. This assumption is not valid if the reaction is slow. The position of the endpoint will be distorted and the results will be inaccurate.

16.6. DIRECT INJECTION ENTHALPIMETRY

When a chemical reaction occurs at constant pressure, heat is liberated or absorbed. The heat flow into or out of a system at constant pressure is quantified using a quantity called enthalpy, H . We usually measure the change in enthalpy, ΔH , called the enthalpy of reaction. It is a reproducible physical property for a given reaction $A + B \rightarrow C + \Delta H$. Therefore the magnitude of ΔH depends on the quantity of reactants involved in the reactions (e.g., multiplying all of the reaction coefficients by 2 means we have to multiply ΔH by 2). Excess amounts of any of the reactants do not take part in the generation or absorption of heat.

Direct injection enthalpimetry (DIE) is similar in many respects to thermometric titrimetry. One essential difference is that an excess of titrant is added very rapidly to the sample and the reactants mixed vigorously. The temperature is then measured against time following the injection of the titrant, as shown in Fig. 16.32. We may suppose that the following exothermic reaction takes place:

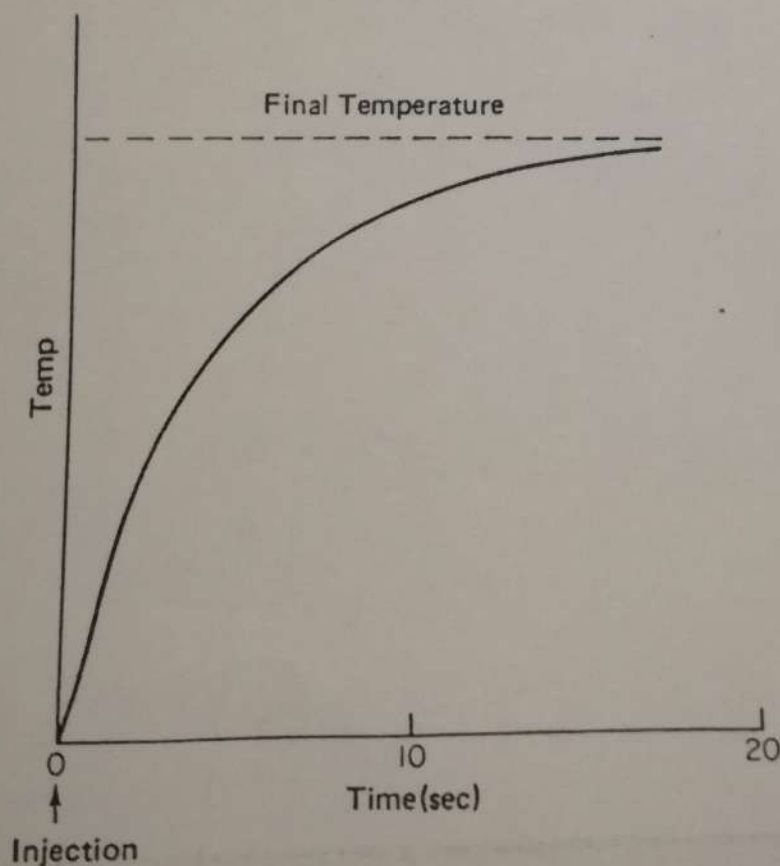
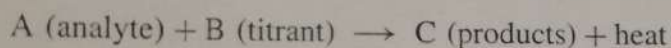


Figure 16.32 DIE titration plot. An excess of reactant B is added rapidly. The amount of analyte A is calculated from the final temperature.

The quantity of heat generated is a function of the number of moles that take part in the reaction. This, in turn, is controlled by the amounts of A and B. Any excess of either A or B does not react. In this instance, we have added an excess of B; therefore the amount of heat generated must be a function of the amount of A present in the mixture. If the amount of A present were halved, then the amount of heat generated would be halved. Since there is an excess of B present in both cases, only the amount of A affects the amount of heat generated.

The method is quite useful, particularly if the rate of chemical reaction between A and B is slow. The final quantity of heat evolved is not a function of time, but a function of the concentration of sample. This is a distinct advantage over conventional volumetric analysis and, in some instances, thermometric titrations. As stated earlier, slow reactions give rise to errors in the endpoint determination in thermometric titrations.

The equipment used for DIE is identical to that for thermometric titrimetry. The titrant must be at the same temperature as the sample at the start of the experiment, and the syringe is emptied rapidly into the cell to deliver the titrant "instantaneously".

DIE may be used for the same applications as discussed for thermometric titrations, for example, for the volumetric analysis of materials, such as boric acid, which are virtually impossible to titrate using endpoint indicators or pH indicators. DIE can also be used in biological studies where the reaction rates may be slow. For example, proteins have been titrated with acid or base, antibodies have been titrated with antigen, and enzyme-coenzyme systems have been studied. DIE is used to determine kinetic parameters for slow reactions. The use of a large excess of one reactant (the titrant) favors the forward reaction (according to Le Chatelier's principle) even if the equilibrium constant is small, so equilibria may be studied using DIE that cannot be studied using other titrimetric methods.

A word of caution should be mentioned about possible interferences, particularly if two simultaneous reactions take place. Since both reactions may generate heat, a direct error will be involved with injection calorimetry methods. However, with thermometric titrations, frequently consecutive reactions take place and can be determined consecutively without prior separation. This has been demonstrated in the titration of calcium and magnesium with oxalate.

16.7. THERMOMECHANICAL ANALYSIS AND DYNAMIC MECHANICAL ANALYSIS

Many materials are used under conditions that subject them to forces or loads. Examples include aluminum alloys used in airplanes, glass in windows and doors, polymers used in molded automobile bumpers, and polymer fibers in "stretch" clothing. The *mechanical* properties of these materials are very important; mechanical properties include ductility, stiffness, hardness and strength. (For an overview of mechanical properties of materials, see an introductory materials science text, such as the one by Callister listed in the bibliography.) The mechanical properties of a material are a function of the applied load, the duration of the load, and environmental conditions, including temperature. The thermal properties of materials are important to understand for the proper selection of materials that will function at elevated or subambient temperatures or for materials exposed to temperature gradients or thermal cycling. The response of mechanical behavior as a function of temperature is studied using **thermomechanical methods of analysis**.

Two important classes of thermomechanical methods of analysis are **thermomechanical analysis (TMA)** and **dynamic mechanical analysis (DMA)**. TMA measures